

Functional Organo-Nano Particles by RAFT Copolymerisation

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Abstract

A significant impact of this work on the use of polymers is expected because the developed organo-nano particles (ONP) mixed into standard polymers will make them unique and traceable. The doping of polymers with non migrating ONP was demonstrated and applications for the recycling of plastics were discussed. Thus, perylene derivatives were linked to polymerisable vinyl groups and copolymerized under RAFT conditions (Reversible Addition Fragmentation chain Transfer) with styrene and methylmethacrylate, respectively, to obtain fluorescent ONP with sizes of 40 nm or even less and narrow distributions of molecular weight in most cases with polydispersities *PD* of 1.1 and lower.

Keywords

Organic Nano Particles (ONP), Reversible Addition Fragmentation Chain Transfer (RAFT), Fluorescence Spectroscopy, Polymers, Recycling

1. Introduction

Nano technology is very promising because of many novel possibilities and is now concentrated to inorganic materials such as titanium dioxide, zinc oxide, alumina and silica. However, the persistency of the majority of such materials is the subject of controversy discussion concerning hazards to human health and environment [1] [2] [3] [4], respectively. A sufficient broad experimental basis for a realistic estimation is still lacking. On the other hand, organic materials are generally long-term degradable where organic nano particles (ONP) would be an attractive alternative for applications in mass products [5]. Moreover, a comparably low lifetime in the environment can be expected because of their large sur-

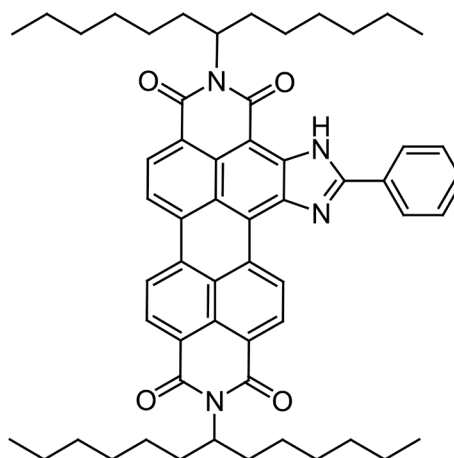
face for chemical and biological attack and degradation; thus, ONP can be estimated as “green materials”. The possibility of the application of ONP found only little attention although the introduction of functionalities such as fluorescent chromophores in organic materials is well-established by the methods of preparative organic chemistry. We prepared fluorescent organo-nano particles in preceding work by polymer analogous reaction [6] with reactive chromophores. A free radical-induced copolymerisation of polymerisable chromophores with various monomers was successful. Nano dimensions were obtained by the application of high concentrations of initiators in rapid reactions [7] where high stationary concentrations of growing chains cause efficient terminations of radicals resulting in short chains and nano dimensions of the polymers. Basically, fluorescent organo-nano particles (ONP) could be prepared by this method, however, with comparably broad distribution of molecular weight and size, respectively. Moreover, the controlling of the reaction was difficult and scaling-up problematic because of the Trommsdorff [8] [9] [10] effect. An easier processing radical reaction leading to a more uniform distribution of size would bring about an appreciable progress.

2. Experimental

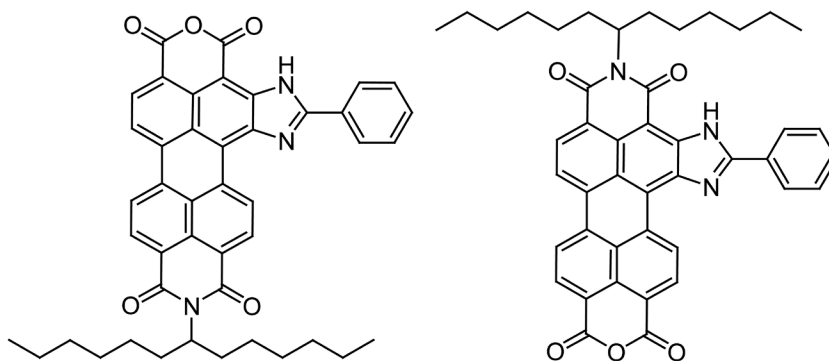
2.1. Spectroscopy

IR spectroscopy: Perkin Elmer BX II FT-IR System with ATR unit. NMR spectra: Varian Vnmrs 600. UV/Vis spectroscopy: Varian Cary 5000. Fluorescence spectra: Varian Cary Eclipse, detector Hamamatsu R3896; fluorescence lifetimes: PicoQuant FluoTime 300; PicoQuant PicoHarp 300 (PC-405 laser; 403 nm). Mass spectra: Finnigan MAT 95, Thermo Finnigan LTQ FT/IonMax, Finnigan JMS-700, Bruker Daltonics Autoflex II (Maldi). Elemental analyses: Elementar vario EL cube. Dynamic light scattering (DLS): Malvern Nano ZS at 633 nm. GPC: Viscotek GPCmax VE-2001. Thermogravimetry: Netzsch STA 440 C TG/DSC. Electron microscopy: Jeol JSM-6500F with EDX detector.

2.2. Chemicals



2,11-Bis(1-hexylheptyl)-5-phenylimidazo[4',5':3,4]anthra[2,1,9-*def*6,5,10-*d'*']diisoquinoline-1,3,10,12(2*H*,11*H*)-tetraone [11]: *N,N*-Bis(1-hexylheptyl)perylene-3,4:9,10-tetracarboxylic-3,4:9,10-bisimide [12] (2.00 g, 2.65 mmol) and freshly prepared fine sodiumamide (2.00 g, 51.3 mmol) were dispersed in benzonitrile (250 mL) heated at 165°C (colour change to blue) for 3 h, allowed to cool, treated with 2 M aqueous HCl (150 mL), extracted with chloroform (150 mL), evaporated in medium vacuum, dissolved in chloroform, filtrated and purified by column separation (silica gel, chloroform/*iso*-hexane 3:1) and precipitated with methanol. Yield 1.62 g (70.1%) dark violet metallic shiny solid, m.p. >250°C. *R_f* (silica gel, chloroform): 0.86. ¹H NMR (CDCl₃/TMS, 600 MHz): δ = 0.78 - 0.89 (m, 12 H, 4 × CH₃), 1.15 - 1.44 (m, 32 H, 16 × CH₂), 1.82 - 1.98 (m, 4 H, 2 × β-CH₂), 2.20 - 2.38 (m, 4 H, 2 × β-CH₂), 5.15 - 5.32 (m, 2 H, α-CH), 7.66 - 7.71 (m, 3 H, 3 × CH_{aryl}), 8.36 (s br., 2 H, 2 × CH_{aryl}), 8.59 - 8.85 (m, 6 H, 6 × CH_{peryl}), 10.79 (d, ³*J*_{H,H} = 7.4 Hz, 1 H; CH_{peryl}), 11.55 ppm (s, 1 H, N-H). MS (DEI⁺/70 eV): *m/z* (%) = 871.5 (50) [*MH*⁺], 870.5 (79) [*M*⁺], 689.3 (19) [*M*⁺ - C₄₄H₄₀O₄N₄], 506.1 (100) [*M*⁺ - C₃₁H₁₄O₄N₄], 390.1 (23) [*M*⁺ - C₂₄H₁₀O₄N₂]. HRMS (C₅₇H₆₆N₄O₄): Calcd. *m/z*: 870.5084, found *m/z*: 870.5091, Δ = 0.0007 mmu.

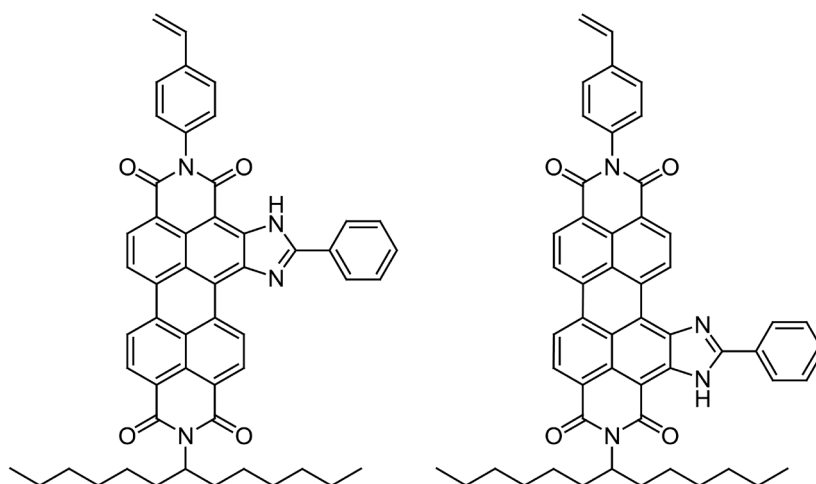


Partial hydrolysis of

2-11-(1-hexylheptyl)-5-phenylimidazo[4',5':3,4]anthra[2,1,9-*def*6,5,10-*d'*']diisoquinoline-1,3,10,12(2*H*,11*H*)-tetraone [11]:

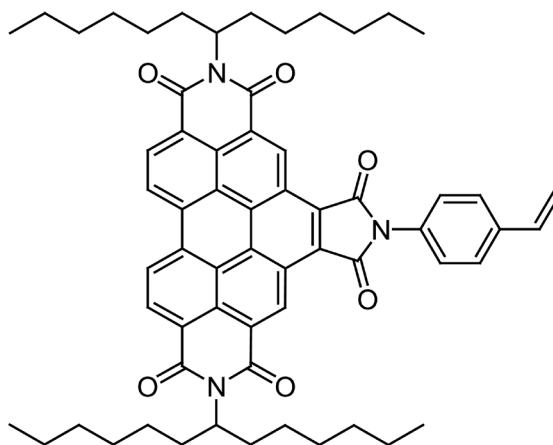
2,11-Bis(1-hexylheptyl)-5-phenylimidazo[4',5':3,4]anthra[2,1,9-*def*6,5,10-*d'*']diisoquinoline-1,3,10,12(2*H*,11*H*)-tetraone (1.49 g, 1.70 mmol) was dispersed in *tert*-butylalcohol (175 mL), heated at 110°C for 1 h (complete dissolution), treated with solid KOH (85%, 2.80 g, 50.0 mmol) refluxed for 4.5 h (bath 110°C), allowed to cool, quenched by means of the addition of 2 M aqueous HCl (100 mL), collected by vacuum filtration, dried at 110°C in air and purified by column separation (silica gel, chloroform/methanol 50:1). Yield 217 mg (19%) dark violet metallic shiny solid, m.p. >250°C. *R_f* (silica gel, chloroform/methanol 50:1): 0.50. ¹H NMR (CDCl₃/TMS, 600 MHz): δ = 0.85 (t, ³*J*_{H,H} = 6.9 Hz, 6 H, 2 × CH₃), 1.19 - 1.48 (m, 16 H, 8 × CH₂), 1.94 - 2.05 (m, 2 H, 2 × β-CH), 2.27 - 2.36 (m, 2 H, 2 × β-CH), 5.15 - 5.31 (m, 1 H, α-CH₂), 7.63 - 7.75 (m, 3 H, 3 × CH_{aryl}), 8.20 (s br., 2 H, 2 × CH_{aryl}), 8.36 - 8.42 (s, 3 H, 3 ×

CH_{per}), 8.47 (d, $^3J_{\text{H,H}} = 8.0$ Hz, 1 H, CH_{per}), 8.52 - 8.62 (m, $^3J_{\text{H,H}} = 7.4$ Hz, 1 H, CH_{per}), 10.41 (d, $^3J_{\text{H,H}} = 8.0$ Hz, 1 H, CH_{per}), 11.33 ppm (s, 1 H, NH). MS (DEI⁺/70 eV): m/z (%) = 690.3 (26) [MH^+], 689.3 (56) [M^+], 507.1 (100) [$M^+ - C_{31}H_{15}O_4N_4$]. HRMS (C₄₄H₃₉N₃O₅): Calcd. m/z : 689.2890, found m/z : 689.2882, $\Delta = 0.0008$ mmu.



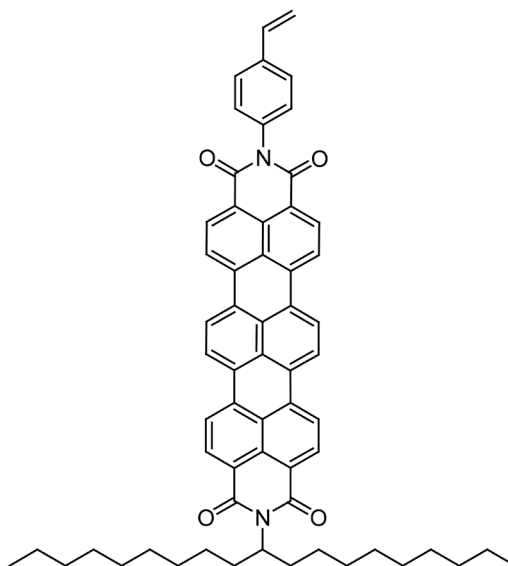
2-(1-Hexylheptyl)-11-(4-vinylphenyl)-5-phenylimidazolo[4',5':3,4]anthra[2,1,9-*def*:6,5,10-*d'e'f'*]diisoquinoline-1,3,10,12(2*H*,11*H*)-tetraone (4a) and 11-(1-hexylheptyl)-2-(4-vinylphenyl)-5-phenylimidazolo[4',5':3,4]anthra[2,1,9-*def*:6,5,10-*d'e'f'*]diisoquinoline-1,3,10,12(2*H*,11*H*)-tetraone (4b) [7]: The mixture of isomers of partially hydrolysed 2,11-(1-hexylheptyl)-5-phenylimidazolo[4',5':3,4]anthra[2,1,9-*def*:6,5,10-*d'e'f'*]diisoquinoline-1,3,10,12(2*H*,11*H*)-tetraone [11] (100 mg, 0.15 mmol), zinc acetate (1 mg) and melt imidazole (1.5 g) were treated with 4-aminostyrene (21 mg, 0.174 mmol), stirred with reflux (bath 120°C) for 3 h (dark violet mixture), allowed to cool, treated with 2 M aqueous HCl, allowed to settle for 1 h, collected by vacuum filtration, dried for 16 h, dissolved in the minimal amount of chloroform, purified by column separation (neutral alumina, CHCl₃/EtOH 100:1), dissolved in the minimal amount of chloroform and precipitated with methanol. Yield 69 mg (60 %) dark violet solid, m.p. 306°C. R_f (silica gel, CHCl₃): 0.52. R_f (silica gel, CHCl₃/EtOH 100:1): 0.63. IR (ATR): $\tilde{\nu}$ = 3412 (w), 3094 (w), 2922 (m), 2854 (m), 1705 (s), 1688 (s), 1657 (s), 1640 (s), 1622 (s), 1590 (s), 1532 (m), 1510 (m), 1485 (w), 1470 (w), 1455 (w), 1430 (w), 1411 (w), 1374 (m), 1343 (s), 1303 (m), 1246 (s), 1191 (m), 1138 (w), 1120 (w), 1053 (w), 1016 (w), 985 (w), 953 (w), 905 (w), 871 (w), 841 (m), 810 (s), 776 (w), 748 (m), 684 cm⁻¹ (s). ¹H NMR (CDCl₃/TMS, 600 MHz): δ = 0.84 (t, $^3J_{\text{H,H}} = 6.4$ Hz, 12 H, 4 × CH₃), 1.21 - 1.47 (m, 24 H, 12 × CH₂), 1.93 - 2.05 (m, 4 H, 2 × β -CH₂), 2.23 - 2.34 (m, 4 H, 2 × β -CH₂), 5.15 - 5.26 (m, 2 H, 2 × α -CH), 5.36 (d, $^3J_{\text{H,H}} = 11.1$ Hz, 1 H, CH_{olef}), 5.39 (d, $^3J_{\text{H,H}} = 11.1$ Hz, 1 H, CH_{olef}), 5.85 (d, $^3J_{\text{H,H}} = 17.8$ Hz, 1 H, CH_{olef}), 5.88 (d, $^3J_{\text{H,H}} = 17.8$ Hz, 1 H, CH_{olef}), 6.83 (dd, $^3J_{\text{H,H}} = 17.7$ Hz, $^3J_{\text{H,H}} = 11.1$ Hz, 1 H, CH_{olef}), 6.85 (dd, $^3J_{\text{H,H}} = 17.7$ Hz, $^3J_{\text{H,H}} = 11.4$ Hz, 1 H, CH_{olef}), 7.36 (d, $^3J_{\text{H,H}} = 8.2$ Hz, 2 H, 2 × CH_{per}), 7.43 (d, $^3J_{\text{H,H}} = 8.2$

Hz, 2 H, $2 \times \text{CH}_{\text{peryl}}$), 7.60 (d, $^3J_{\text{H,H}} = 8.2$ Hz, 2 H, $2 \times \text{CH}_{\text{peryl}}$), 7.62 - 7.70 (m, 8 H, $8 \times \text{CH}_{\text{arom}}$), 8.01 (d, $^3J_{\text{H,H}} = 5.8$ Hz, 2 H, $2 \times \text{CH}_{\text{peryl}}$), 8.11 - 8.65 (m, 12 H, $12 \times \text{CH}_{\text{arom}}$), 10.27 (s, 1 H; CH_{peryl}), 10.40 (s, 1 H; CH_{peryl}), 11.10 ppm (s, 1 H, N-H), 11.27 ppm (s, 1 H, N-H). ^{13}C NMR (CDCl_3/TMS , 150 MHz): $\delta = 163.67$, 138.66, 138.19, 136.44, 134.70, 132.44, 132.01, 129.58, 129.02, 127.99, 127.29, 115.07, 32.59, 31.99, 29.48, 29.47, 29.46, 27.31, 22.81, 22.79, 14.25, 14.23 ppm. UV/Vis (CHCl_3): λ_{max} (ϵ) = 459 (12600), 466 (14600), 508 (15600), 544 (45000), 589 nm (85800). Fluorescence (CHCl_3 , $\lambda_{\text{exc}} = 544$ nm): λ_{max} (I_{rel}): 601 (1.0), 654 (0.48), 714 nm (0.12). Fluorescence quantum yield (CHCl_3 , $\lambda_{\text{exc}} = 544$ nm, $E_{544 \text{ nm/1 cm}} = 0.0093$, reference: S-13, registry number RN 110590-84-6, with $\Phi = 1.00$): $\Phi = 0.89$. MS (DEI^+ , 70 eV): m/z (%) = 790.4 (10) [M^+], 608.1 (21) [$M^+ - \text{C}_{39}\text{H}_{20}\text{O}_4\text{N}_4$], 461.1 (12) [$M^+ - \text{C}_{35}\text{H}_{13}\text{N}_2$], 182.2 (34) [$M^+ - \text{C}_{13}\text{H}_{26}$], 69.1 (100). HRMS ($\text{C}_{52}\text{H}_{46}\text{N}_4\text{O}_4$): Calcd. m/z : 790.3519, found m/z : 790.3516, $\Delta = 0.0003$ mmu. $\text{C}_{52}\text{H}_{46}\text{N}_4\text{O}_4$ (790.4): Calcd. C 78.96, H 5.86, N 7.08; found C 78.63, H 6.03, N 6.98.



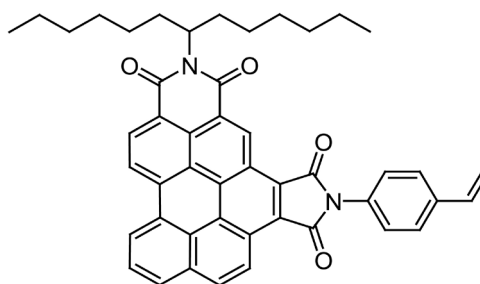
2,10-Bis(1-hexylheptyl)-6-(4-vinylphenyl)-1H-pyrrolo[3',4':4,5]pyreno[2,1,10-def:7,8,9-d'e'f]diisoquinoline-1,3,5,7,9,11(2H,6H,10H)-hexone (6) [7]: *N,N'*-Bis(1-hexylheptyl)benzo[ghi]perylene-2,3,8,9,11,12-hexacarboxylic-2,3,8,9-bis(dicarboximide)-11,12-anhydride [17] (0.40 g, 0.47 mmol), zinc acetate (5 mg) and melt imidazole (7.0 g) were treated with 4-aminostyrene (70 mg, 0.59 mmol), stirred under reflux (bath 120°C) for 3 h (ochre mixture), allowed to cool, treated with 2 M aqueous HCl, allowed to settle for 1 h, collected by vacuum filtration (ochre solid), dried for 16 h, dissolved in the minimal amount of chloroform, purified by column separation (neutral alumina, $\text{CHCl}_3/\text{EtOH}$ 100:1) dissolved in the minimal amount of chloroform and precipitated with methanol. Yield 221 mg (49%) yellowish orange solid, m.p. >300°C. R_f (silica gel, CHCl_3): 0.82. R_f (silica gel, $\text{CHCl}_3/\text{EtOH}$ 100:1): 0.91. IR (ATR): $\tilde{\nu} = 3074$ (w), 2953 (m), 2924 (m), 2855 (m), 1772 (w), 1707 (s), 1662 (s), 1626 (w), 1595 (m), 1513 (m), 1457 (m), 1413 (m), 1391 (m), 1363 (s), 1315 (s), 1292 (m), 1275 (m), 1241 (m), 1202 (w), 1177 (w), 1156 (w), 1123 (w), 1102 (w), 1029 (w), 1017 (w), 987 (w), 961 (w), 944 (m), 908 (w), 880 (m), 845 (m), 811 (m), 797 (w), 779 (w),

764 (m), 747 (w), 724 (w), 698 (w), 659 cm^{-1} (w). ^1H NMR (CDCl_3/TMS , 600 MHz): δ = 0.84 (t, $^3J_{\text{H,H}}$ = 6.8 Hz, 12 H, $4 \times \text{CH}_3$), 1.23 - 1.55 (m, 32 H, $16 \times \text{CH}_2$), 1.95 - 2.05 (m, 4 H, $2 \times \beta\text{-CH}_2$), 2.30 - 2.41 (m, 4 H, $2 \times \beta\text{-CH}_2$), 5.25 - 5.35 (m, 2 H, NCH), 5.40 (d, $^3J_{\text{H,H}}$ = 11.0 Hz, 1 H, CH_{olef}), 5.91 (d, $^3J_{\text{H,H}}$ = 17.7 Hz, 1 H, CH_{olef}), 6.87 (dd, $^3J_{\text{H,H}}$ = 17.6 Hz, $^3J_{\text{H,H}}$ = 10.9 Hz, 1 H, CH_{olef}), 7.71 (d, $^3J_{\text{H,H}}$ = 7.9 Hz, 2 H, CH_{arom}), 7.74 (d, $^3J_{\text{H,H}}$ = 8.0 Hz, 2 H, CH_{arom}), 9.06 (s, 4 H, $4 \times \text{CH}_{\text{pery}}$), 10.21 ppm (s, 2 H, CH_{pery}). ^{13}C NMR (CDCl_3/TMS , 150 MHz): δ = 166.81, 137.79, 136.27, 132.63, 130.73, 127.40, 127.16, 126.96, 126.72, 124.43, 123.68, 122.75, 115.27, 55.54, 32.57, 31.97, 29.46, 27.27, 22.79, 14.23 ppm. UV/Vis (CHCl_3): λ_{max} (ϵ) = 379 (32300), 410 (20400), 436 (38100), 467 nm (56800). Fluorescence (CHCl_3 , λ_{exc} = 436 nm): λ_{max} (I_{rel}): 477 (1.0), 511 nm (0.84). Fluorescence quantum yield (CHCl_3 , λ_{exc} = 436 nm, $E_{436 \text{ nm}/1 \text{ cm}}$ = 0.0188, reference: S-13 with Φ = 1.00): Φ = 0.03. MS (DEI^+ , 70 eV): m/z (%) = 950.5 (10) [$M\text{H}^+$], 586.1 (32) [M^+ - $\text{C}_{36}\text{H}_{16}\text{O}_6\text{N}_3$], 69.1 (100). HRMS ($\text{C}_{62}\text{H}_{68}\text{N}_3\text{O}_6$): Calcd. m/z 950.5108, found m/z 950.5112, Δ = 0.0004 mmu. $\text{C}_{62}\text{H}_{67}\text{N}_3\text{O}_6$ (949.5): Calcd. C 78.37, H 7.11, N 4.42; found C 78.46, H 7.23, N 4.35.



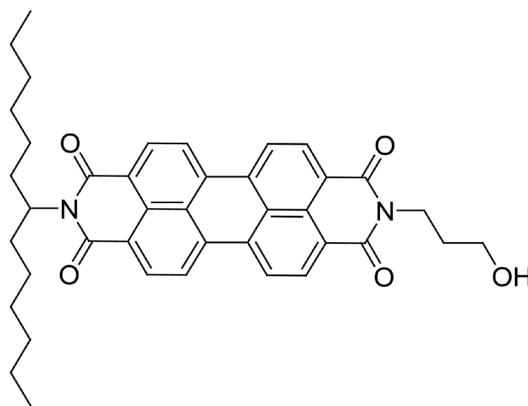
2-(1-Nonyldecyl)-11-(4-vinylphenyl)benzo[13,14]pentapheno[3,4,5-*def*:10,9,8-*d'e'f'*]diisoquinoline-1,3,10,12(2*H*,11*H*)-tetraone (5): 11-(1-Nonyldecyl)-1*H*-benzo[13,14]isochromeno[6',5',4':8,9,10]pentapheno[3,4,5-*def*]isoquinoline-1,3,10,12(11*H*)-tetraon [18] (48 mg, 0.062 mmol), zinc acetate (1 mg) and melt imidazole (800 mg) were treated with 4-aminostyrene (9.6 mg, 0.081 mmol), stirred under reflux (bath 120°C) for 3 h (dark blue mixture), allowed to cool, treated with 2 M aqueous HCl, allowed to settle for 1 h, dried for 16 h, dissolved in the minimal amount of chloroform, purified by column separation (neutral alumina, $\text{CHCl}_3/\text{EtOH}$ 100:1), dissolved in the minimal amount of chloroform and precipitated with methanol. Yield 19 mg (35%) dark blue solid, m.p. > 250°C. R_f (silica gel, CHCl_3): 0.32. R_f (silica gel, $\text{CHCl}_3/\text{EtOH}$ 100:1): 0.56. IR (ATR): $\tilde{\nu}$ = 2919 (s), 2850 (m), 1692 (s), 1650 (s), 1584 (s), 1504 (w), 1452 (w),

1378 (w), 1354 (s), 1327 (w), 1305 (w), 1315 (s), 1252 (w), 1209 (w), 1184 (w), 1143 (w), 1016 (w), 913 (w), 840 (w), 807 (s), 780 (w), 748 (m), 722 (w) 695 (m), 679 cm^{-1} (w). ^1H NMR (CDCl_3/TMS , 600 MHz): δ = 0.80 - 0.92 (m, 6 H, $2 \times \text{CH}_3$), 1.15 - 1.40 (m, 28 H, $14 \times \text{CH}_2$), 1.84 - 1.93 (m, 2 H, $1 \times \beta\text{-CH}_2$), 2.24 - 2.32 (m, 4 H, $2 \times \beta\text{-CH}_2$), 5.14.25 (m, 1 H, NCH), 5.35 (d, $^3J_{\text{H,H}} = 10.8$ Hz, 1 H, CH_{olef}), 5.84 (d, $^3J_{\text{H,H}} = 17.3$ Hz, 1 H, CH_{olef}), 6.82 (dd, $^3J_{\text{H,H}} = 17.5$ Hz, $^3J_{\text{H,H}} = 10.9$ Hz, 1 H, CH_{olef}), 7.34 (d, $^3J_{\text{H,H}} = 8.2$ Hz, 2 H, CH_{arom}), 7.61 (d, $^3J_{\text{H,H}} = 8.9$ Hz, 2 H, CH_{arom}), 8.47 - 8.76 ppm (m, 12 H, $12 \times \text{CH}_{\text{Terry}}$). UV/Vis (CHCl_3): λ_{max} (E_{rel}) = 560 (0.18), 600 (0.52), 656 nm (1.00). Fluorescence (CHCl_3 , $\lambda_{\text{exc}} = 601$ nm): λ_{max} (I_{rel}): 671 (1.00), 735 nm (0.46). Fluorescence quantum yield (CHCl_3 , $\lambda_{\text{exc}} = 600$ nm, $E_{600\text{nm}/1\text{cm}} = 0.0100$, reference: S-13 with $\Phi = 1.00$): $\Phi = 0.45$. MS (DEI $^+$, 70 eV): m/z (%) = 883.4 (19) [$M\text{H}^+$], 616.1 (100) [$M^+ - \text{C}_{42}\text{H}_{20}\text{O}_4\text{N}_2$], 156.2 (60) [$M^+ - \text{C}_{10}\text{H}_{22}\text{N}_1$]. HRMS ($\text{C}_{61}\text{H}_{59}\text{N}_2\text{O}_4$): Calcd. m/z 883.4475, found m/z 883.4497, $\Delta = 0.0022$ mmu.



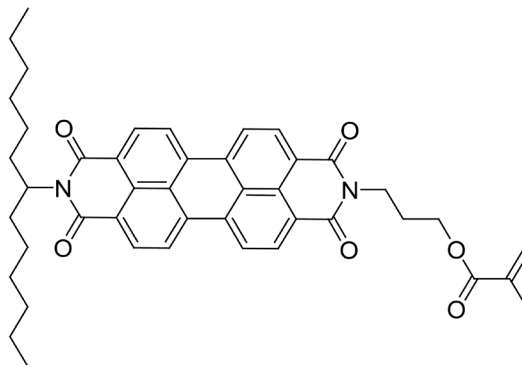
11-(1-Hexylheptyl)-7-(4-vinylphenyl)benzo[8,9]pyrrolo[3',4':4,5]pyreno[2,1,10-*def*]isoquinoline-6,8,10,12(7*H*,11*H*)-tetrone (7): *N*-(1-Hexylheptyl)benzo[*ghi*]perylene-3,4:6,7-tetracarboxylic-3,4-dicarboximide-6,7-anhydride [22] (140 mg, 0.23 mmol), zinc acetate (1.0 mg) and melt imidazole (1.5 g) were treated with 4-aminostyrene (37 mg, 0.31 mmol), stirred under reflux (bath 120°C) for 3 h (orange mixture), allowed to cool, treated with 2 M aqueous HCl, allowed to settle for 1 h, dried for 16 h, dissolved in the minimal amount of chloroform and purified by column separation (neutral alumina, $\text{CHCl}_3/\text{EtOH}$ 100:1), dissolved in the minimal amount of chloroform and precipitated with methanol. Yield 67 mg (48%) yellowish orange solid, m.p. 248°C. R_f (silica gel, CHCl_3): 0.68. R_f (silica gel, $\text{CHCl}_3/\text{EtOH}$ 100:1): 0.88. IR (ATR): $\tilde{\nu}$ = 2924 (m), 2855 (m), 1766 (w), 1713 (s), 1659 (s), 1623 (w), 1604 (m), 1581 (w), 1513 (m), 1456 (w), 1422 (w), 1370 (s), 1323 (s), 1290 (m), 1245 (m), 1223 (w), 1204 (w), 1177 (w), 1159 (m), 1120 (m), 1094 (m), 991 (w), 940 (w), 886 (w), 838 (s), 811 (s), 765 (m), 751 (m), 725 (w), 664 cm^{-1} (w). ^1H NMR (CDCl_3/TMS , 600 MHz): δ = 0.85 (t, $^3J_{\text{H,H}} = 7.1$ Hz, 6 H, $2 \times \text{CH}_3$), 1.22 - 1.52 (m, 16 H, $8 \times \text{CH}_2$), 1.97 - 2.07 (m, 2 H, $1 \times \beta\text{-CH}_2$), 2.32 - 2.42 (m, 4 H, $2 \times \beta\text{-CH}_2$), 5.27 - 5.34 (m, 1 H, NCH), 5.41 (d, $^3J_{\text{H,H}} = 11.1$ Hz, 1 H, CH_{olef}), 5.91 (d, $^3J_{\text{H,H}} = 17.7$ Hz, 1 H, CH_{olef}), 6.87 (dd, $^3J_{\text{H,H}} = 17.6$ Hz, $^3J_{\text{H,H}} = 10.9$ Hz, 1 H, CH_{olef}), 7.70 (s, 3 H, CH_{arom}), 8.13 (d, $^3J_{\text{H,H}} = 7.6$ Hz, 1 H, CH_{arom}), 8.18 (d, $^3J_{\text{H,H}} = 8.8$ Hz, 1 H, CH_{arom}), 8.30 (d, $^3J_{\text{H,H}} = 7.6$ Hz, 1 H, CH_{arom}), 8.86 - 8.97 (m, 3 H, $3 \times \text{CH}_{\text{arom}}$), 9.08 (d, $^3J_{\text{H,H}} = 8.9$ Hz, 1 H,

CH_{arom}), 9.97 ppm (s, 1 H, CH_{arom}). ¹³C NMR (CDCl₃/TMS, 150 MHz): δ = 167.83, 136.27, 132.22, 131.92, 131.09, 130.02, 128.59, 128.54, 127.65, 127.15, 126.73, 126.14, 125.43, 124.23, 123.97, 123.85, 123.09, 122.34, 121.99, 121.83, 115.23, 110.17, 32.02, 29.52, 27.35, 22.82, 14.25 ppm. UV/Vis (CHCl₃): $\lambda_{\max}$ (ϵ) = 263 (46900), 353 (26900), 368 (46600), 416 (19200), 439 (38100), 480 nm (7000). Fluorescence (CHCl₃, λ_{exc} = 353 nm): $\lambda_{\max}$ (I_{rel}): 503 nm (1.0). Fluorescence quantum yield (CHCl₃, λ_{exc} = 353 nm, $E_{353\text{nm}/1\text{cm}}$ = 0.0351, reference: S-13 with Φ = 1.00): Φ = 0.07. MS (DEI⁺, 70 eV): m/z (%) = 699.3 (2) [M^+], 516.1 (19) [M^+ – C₃₄H₁₆O₄N₂], 343.1 (5) [M^+ – C₂₄H₉O₂N₁], 182.2 (39) [M^+ – C₁₃H₂₆], 69.1 (100). HRMS (C₄₇H₄₃N₂O₄): Calcd. m/z : 699.3223, found m/z : 699.3224, Δ = 0.0001 mmu. C₄₇H₄₂N₂O₄ (698.3): Calcd. C 80.78, H 6.06, N 4.01; found C 80.56, H 6.16, N 4.02.



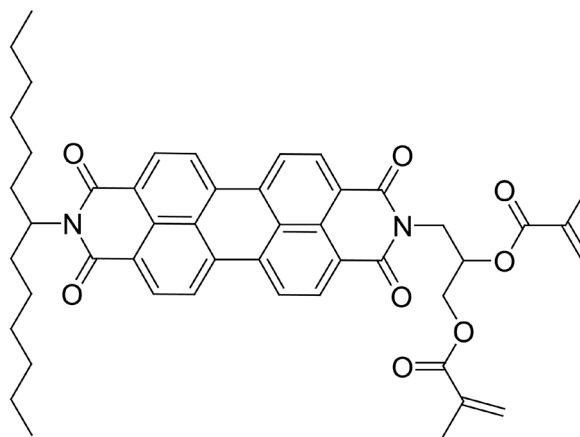
***N*-(1-Hexylheptyl)-*N'*-(3-hydroxypropyl)perylene-3,4:9,10-tetracarboxylic bisimide:** 9-(1-Hydroxypropyl)-2-benzopyrano[6',5':10,5,6]anthra[2,1,9-*def*]isoquinoline-1,3,8,10-tetraone (2.90 g, 6.45 mmol) and imidazole (8.0 g) were heated at 140 °C, treated with 1-hexylheptylamine (2.57 g, 12.9 mmol), further heated for 2 h, allowed to cool, still warm treated with 2 M aqueous HCl, allowed to cool, collected by vacuum filtration, dried at 110 °C for 16 h, purified by column separation (silica gel, chloroform/ethanol 30:1), dissolved in the minimal amount of chloroform and precipitated with methanol. Yield 2.37 g (58 %) red solid, m.p. 308 °C. R_f (silica gel, chloroform/ethanol 20:1): 0.48. IR (ATR): $\tilde{\nu}$ = 3480 (w), 2953 (w), 2923 (m), 2855 (m), 1690 (s), 1642 (s), 1593 (s), 1577 (m), 1506 (w), 1479 (w), 1466 (w), 1456 (w), 1439 (m), 1404 (m), 1375 (w), 1353 (s), 1336 (s), 1268 (m), 1246 (s), 1218 (m), 1196 (m), 1179 (m), 1166 (m), 1126 (m), 1107 (w), 1097 (w), 1079 (m), 1054 (w), 1037 (w), 983 (m), 967 (m), 936 (w), 916 (w), 891 (w), 864 (m), 846 (m), 822 (w), 809 (s), 796 (m), 764 (w), 759 (w), 747 (s), 727 (m), 696 (w), 665 cm⁻¹ (w). ¹H NMR (CDCl₃/TMS, 600 MHz): δ = 0.83 (t, ³ $J_{\text{H,H}}$ = 6.9 Hz, 6 H, 2 × CH₃), 1.19 - 1.40 (m, 16 H, 8 × CH₂), 1.85 - 1.93 (m, 2 H, β -CH₂), 2.03 (q, ³ $J_{\text{H,H}}$ = 5.8 Hz, 2 H, CH₂), 2.20 - 2.29 (m, 2 H, β -CH₂), 3.02 (t, ³ $J_{\text{H,H}}$ = 6.8 Hz, 1 H, OH), 3.64 (dd, ³ $J_{\text{H,H}}$ = 11.6 Hz, ³ $J_{\text{H,H}}$ = 6.0 Hz, 2 H, CH₂-O), 4.36 (t, ³ $J_{\text{H,H}}$ = 6.2 Hz, 2 H, CH₂-N), 5.14 - 5.22 (m, 1 H, α -CH), 8.46 - 8.66 ppm (m, 8 H, 8 × CH_{perylene}). ¹³C NMR (CDCl₃/TMS, 150 MHz): δ = 164.07, 135.03,

134.12, 131.72, 129.50, 126.44, 126.30, 123.33, 123.01, 122.77, 59.18, 55.03, 37.22, 32.52, 31.92, 31.15, 29.38, 27.12, 22.74, 14.20 ppm. UV/Vis (CHCl_3): λ_{max} (ϵ_{rel}) = 461 (0.22), 491 (0.60), 527 nm (1.0). Fluorescence (CHCl_3 , λ_{exc} = 490 nm): λ_{max} (I_{rel}): 535 (1.0), 579 (0.50), 628 nm (0.12). Fluorescence quantum yield (CHCl_3 , λ_{exc} = 490 nm, $E_{490\text{nm}/1\text{cm}}$ = 0.0100, reference: S-13 with Φ = 1.00): Φ = 0.97. MS (DEI+, 70 eV): m/z (%) = 631.3 (44) [$M\text{H}^+$], 630.3 (90) [M^+], 448.1 (100) [$M^+ - \text{C}_{27}\text{H}_{16}\text{O}_5\text{N}_2$], 391.1 (46) [$M^+ - \text{C}_{24}\text{H}_{11}\text{O}_4\text{N}_2$]. HRMS ($\text{C}_{40}\text{H}_{42}\text{N}_2\text{O}_5$): Calcd. m/z : 630.3094, found m/z : 630.3092, Δ = 0.0002 mmu. $\text{C}_{40}\text{H}_{42}\text{N}_2\text{O}_5$ (630.3): Calcd. C 76.17, H 6.71, N 4.44; found C 75.84, H 6.60, N 4.43.



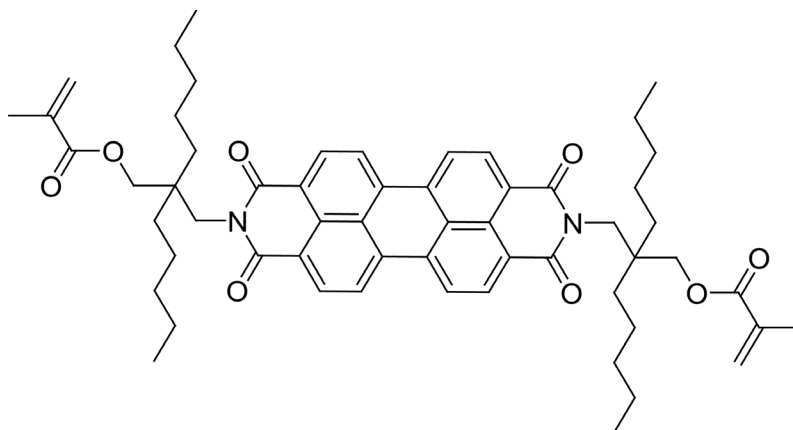
***N*-(1-Hexylheptyl)-*N'*-(3-methacryloyloxypropyloxy)perylene-3,4:9,10-tetracarboxbisimide (8):** Toluene (45 mL) and *N*-(1-hexylheptyl)-*N'*-(3-hydroxypropyl)perylene-3,4:9,10-tetracarboxbisimide (850 mg, 1.36 mmol) were stirred under argon atmosphere, treated with triethylamine (680 mg, 7.90 mmol) and methacryloylchloride (700 mg, 7.90 mmol), stirred at 20°C for 16 h, evaporated in vacuo, purified by column separation (silica gel, chloroform/acetone 100:1), dissolved in the minimal amount of chloroform, precipitated with methanol, collected by vacuum filtration and dried at 110°C for 16 h. Yield 540 mg (57 %) red solid, m.p. 218°C. R_f (silica gel, chloroform/acetone 100:1): 0.54. IR (ATR): $\tilde{\nu}$ = 2956 (w), 2925 (w), 2856 (w), 1695 (s), 1658 (s), 1646 (s), 1594 (m), 1578 (m), 1506 (w), 1482 (w), 1454 (w), 1439 (m), 1404 (m), 1378 (w), 1354 (m), 1340 (s), 1296 (m), 1252 (m), 1216 (w), 1173 (m), 1126 (w), 1109 (w), 1070 (w), 1034 (w), 1012 (w), 959 (w), 942 (w), 892 (w), 852 (w), 810 (s), 796 (w), 769 (w), 745 (s), 726 (w), 696 cm^{-1} (w). ^1H NMR (CDCl_3/TMS , 600 MHz): δ = 0.82 (t, $^3J_{\text{H,H}}$ = 7.0 Hz, 6 H, $2 \times \text{CH}_3$), 1.18 - 1.38 (m, 16 H, $8 \times \text{CH}_2$), 1.83 - 1.91 (m, 2 H, $\beta\text{-CH}_2$), 1.94 (s, 3 H, CH_3), 2.16 - 2.29 (m, 4 H, $\beta\text{-CH}_2$, $1 \times \text{CH}_2$), 4.30 (t, $^3J_{\text{H,H}}$ = 6.2 Hz, 2 H, $\text{CH}_2\text{-O}$), 4.37 (t, $^3J_{\text{H,H}}$ = 7.2 Hz, 2 H, $\text{CH}_2\text{-N}$), 5.16 - 5.21 (m, 1 H, $\alpha\text{-CH}$), 5.52 (s, 1 H, $\text{CH}_2 = \text{C}$), 6.12 (s, 1 H, $\text{CH}_2 = \text{C}$), 8.60 - 8.72 ppm (m, 8 H, $8 \times \text{CH}_{\text{perylene}}$). ^{13}C NMR (CDCl_3/TMS , 150 MHz): δ = 167.51, 163.57, 136.43, 135.07, 131.71, 129.72, 129.63, 126.71, 126.57, 125.65, 123.37, 123.22, 123.17, 62.71, 54.97, 37.93, 32.53, 31.91, 29.86, 29.36, 27.59, 27.08, 22.73, 18.45, 14.20 ppm. UV/Vis (CHCl_3): λ_{max} (ϵ) = 459 (14900), 490 (44600), 527 nm (76400). Fluorescence (CHCl_3 , λ_{exc} = 490 nm): λ_{max} (I_{rel}): 535 (1.0), 579 (0.50), 627 nm (0.12). Fluorescence quantum yield (CHCl_3 , λ_{exc} = 490 nm, $E_{490\text{nm}/1\text{cm}}$ =

0.0835, reference: S-13 with $\Phi = 1.00$): $\Phi = 1.00$. MS (DEI+, 70 eV): m/z (%) = 699.3 (49) [MH^+], 698.3 (96) [M^+], 517.1 (100) [$M^+ - C_{31}H_{21}O_6N_2$], 391.1 (100) [$M^+ - C_{24}H_{11}N_2O_4$]. HRMS ($C_{44}H_{46}N_2O_6$): Calcd. m/z 698.3356, found m/z 698.3343, $\Delta = 0.0013$ mmu. $C_{44}H_{46}N_2O_6$ (698.3): Calcd. C 75.62, H 6.63, N 4.01; found C 75.06, H 6.64, N 3.93.



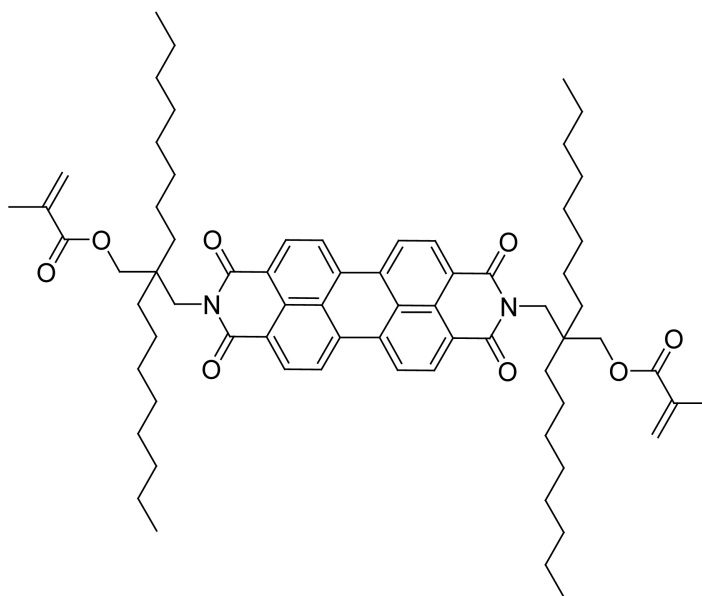
***N*-(1-Hexylheptyl)-*N'*-(2,3-bis-methacroyloxypropyloxy)perylene-3,4:9,10-tetracarboxbisimide (9):** Chloroform (12 mL) and *N*-(1-hexylheptyl)-*N'*-(2,3-dihydroxypropyl)perylene-3,4:9,10-tetracarboxbisimide [23] (290 mg, 0.45 mmol) were stirred under argon atmosphere, treated with triethylamine (450 mg, 4.49 mmol) and methacroylchloride (510 mg, 4.49 mmol), stirred at 40 °C for 4 d, evaporated in vacuo, purified by column separation (alumina, chloroform/ethanol 100:1), precipitated from a concentrated solution in chloroform with methanol and dried at 80 °C for 16 h. Yield 244 mg (69 %) red solid, m.p. 122 °C. R_f (silica gel, chloroform/ethanol 20:1): 0.89. IR (ATR): $\tilde{\nu}$ = 2955 (w), 2925 (m), 2856 (w), 1695 (s), 1655 (s), 1593 (s), 1578 (m), 1507 (w), 1483 (w), 1453 (m), 1436 (m), 1404 (m), 1377 (w), 1340 (s), 1294 (m), 1250 (m), 1221 (w), 1172 (s), 1148 (s), 1127 (m), 1107 (m), 1063 (m), 1009 (m), 941 (m), 852 (m), 809 (s), 785 (m), 746 (s), 722 cm^{-1} (m). 1H NMR ($CDCl_3$ /TMS, 600 MHz): δ = 0.83 (t, $^3J_{H,H} = 7.1$ Hz, 6 H, $2 \times CH_3$), 1.20 - 1.42 (m, 16 H, $8 \times CH_2$), 1.83 (s, 3 H, CH_3), 1.87 - 1.95 (m, 2 H, $\beta-CH_2$), 1.97 (s, 3 H, CH_3), 2.21 - 2.29 (m, 2 H, $\beta-CH_2$), 4.36 (dd, $^3J_{H,H} = 14.0$ Hz, $^1J_{H,H} = 3.9$ Hz, 1 H, CH_2-N), 4.42 (dd, $^3J_{H,H} = 11.9$ Hz, $^1J_{H,H} = 5.7$ Hz, 1 H, CH_2-O), 4.52 (dd, $^3J_{H,H} = 11.9$ Hz, $^1J_{H,H} = 3.8$ Hz, 1 H, CH_2-O), 4.69 (dd, $^3J_{H,H} = 14.0$ Hz, $^1J_{H,H} = 8.1$ Hz, 1 H, CH_2-N), 5.14 - 5.20 (m, 1 H, $\alpha-CH$), 5.48 - 5.54 (m, 1 H, $CH = C$), 5.58 - 5.64 (m, 2 H, $CH = C$, $CH_2-CHO-CH_2$), 6.05 (s, 1 H, $CH = C$), 6.18 (s, 1 H, $CH = C$), 8.15 (d, $^3J_{H,H} = 8.1$ Hz, 2 H, $2 \times CH_{\text{perylene}}$), 8.23 (d, $^3J_{H,H} = 8.1$ Hz, 2 H, $2 \times CH_{\text{perylene}}$), 8.31 (d, $^3J_{H,H} = 7.9$ Hz, 2 H, $2 \times CH_{\text{perylene}}$), 8.47 ppm (d, $^3J_{H,H} = 12.5$ Hz, 2 H, $2 \times CH_{\text{perylene}}$). ^{13}C NMR ($CDCl_3$ /TMS, 101 MHz): δ = 166.97, 166.87, 163.04, 135.94, 135.89, 134.30, 133.62, 131.10, 129.19, 129.00, 126.42, 126.37, 125.89, 125.77, 122.86, 122.64, 122.46, 70.07, 63.85, 54.98, 40.71, 30.46, 31.90, 29.36, 27.14, 22.71, 18.40, 18.31, 14.17 ppm. UV/Vis ($CHCl_3$): λ_{max} (ϵ) = 459 (20,900), 490 (55,500), 527 nm

(92,700). Fluorescence (CHCl_3 , $\lambda_{\text{exc}} = 490 \text{ nm}$): λ_{max} (I_{rel}): 534 (1.0), 576 (0.50), 625 nm (0.11). Fluorescence quantum yield (CHCl_3 , $\lambda_{\text{exc}} = 490 \text{ nm}$, $E_{490\text{nm}/1\text{cm}} = 0.0881$, reference: S-13 with $\Phi = 1.00$): $\Phi = 0.92$. MS (DEI⁺, 70 eV): m/z (%) = 783.4 (55) [MH^+], 782.4 (100) [M^+], 601.2 (62) [$M^+ - C_{35}H_{25}O_8N_2$], 429.1 (100) [$M^+ - C_{24}H_{15}O_7N_1$]. HRMS ($C_{48}H_{50}N_2O_8$): Calcd. m/z 782.3567, found m/z 782.3560, $\Delta = 0.0007 \text{ mmu}$. $C_{48}H_{50}N_2O_8$ (646.3): Calcd. C 73.64, H 6.44, N 3.58; found C 73.40, H 6.46, N 3.57.



2,9-Bis-[2-(methacryloyloxymethoxy)-2-pentylheptyl]anthra[2,1,9-*def*6,5,10-*d'e'f'*]diisoquinoline-1,3,8,10-tetraone (10): Toluene (50 mL) and 2,9-bis-[2-(hydroxymethyl)-2-pentylheptyl]anthra[2,1,9-*def*6,5,10-*d'e'f'*]diisoquinoline-1,3,8,10-tetraone [24] (1.00 g, 1.27 mmol) were stirred under argon atmosphere, treated with triethylamine (1.29 g, 12.7 mmol) and methacryloylchloride (1.33 g, 12.7 mmol), stirred at 20°C for 3 d, treated with further methacryloylchloride (2.0 g) and chloroform (10 mL), stirred for 16 h, treated with further methacryloylchloride (1 g), stirred at 35°C for 6 h, evaporated in vacuo, purified by column separation (silica gel, chloroform/acetone 100:1), dissolved in the minimal amount of chloroform, precipitated with methanol, collected by vacuum filtration and dried at 110°C for 16 h. Yield 680 mg (58 %) red solid, m.p. 152°C. R_f (silica gel, chloroform/acetone 100:1): 0.37. IR (ATR): $\tilde{\nu} = 2954 \text{ (m)}$, 2929 (m), 2860 (w), 1699 (s), 1659 (s), 1594 (s), 1578 (m), 1507 (w), 1454 (m), 1436 (m), 1404 (m), 1376 (m), 1335 (s), 1295 (s), 1248 (m), 1217 (m), 1160 (s), 1126 (m), 1068 (w), 1013 (m), 989 (m), 935 (m), 892 (w), 853 (m), 834 (w), 809 (s), 795 (m), 747 (s), 725 (m), 672 cm^{-1} (w). ^1H NMR (CDCl_3/TMS , 600 MHz): $\delta = 0.88$ (t, $^3J_{\text{H,H}} = 7.1 \text{ Hz}$, 12 H, $6 \times \text{CH}_3$), 1.21 - 1.51 (m, 32 H, $16 \times \text{CH}_2$), 1.69 (s, 6H, $2 \times \text{CH}_3$), 4.09 (s, 4 H, $2 \times \text{CH}_2\text{-O}$), 4.34 (s, 4 H, $2 \times \text{CH}_2\text{-N}$), 5.16 - 5.19 (m, 1 H, $\text{CH} = \text{C}$), 5.80 (s, 1 H, $\text{CH} = \text{C}$), 8.52 - 8.66 ppm (m, 8 H, $8 \times \text{CH}_{\text{pery}}$). ^{13}C NMR (CDCl_3/TMS , 101 MHz): $\delta = 167.24$, 164.29, 136.49, 134.65, 131.70, 129.36, 126.46, 124.88, 123.49, 123.18, 69.26, 45.35, 41.84, 33.91, 32.96, 22.97, 22.73, 18.24, 14.20 ppm. UV/Vis (CHCl_3): λ_{max} (ϵ) = 459 (20700), 488 (52900), 525 nm (84500). Fluorescence (CHCl_3 , $\lambda_{\text{exc}} = 490 \text{ nm}$): λ_{max} (I_{rel}): 533 (1.0), 575 (0.50), 624 nm (0.11). Fluorescence quantum yield (CHCl_3 , $\lambda_{\text{exc}} = 490 \text{ nm}$, $E_{490\text{nm}/1\text{cm}} =$

0.0745, reference: S-13 with $\Phi = 1.00$): $\Phi = 0.88$. MS (DEI⁺, 70 eV): m/z (%) = 923.5 (59) [MH^+], 922.5 (84) [M^+], 657.3 (27) [$M^+ - C_{41}H_{41}O_6N_2$], 404.1 (56) [$M^+ - C_{25}H_{12}O_4N_2$]. HRMS ($C_{58}H_{70}N_2O_8$): Calcd. m/z 922.5132, found m/z 922.5115, $\Delta = 0.0017$ mmu. $C_{58}H_{70}N_2O_8$ (922.5): Calcd. C 75.46, H 7.64, N 3.03; found C 75.37, H 7.61, N 2.99.



2,9-Bis-[2-(methacryloyloxymethoxy)-2-octyldecyl]anthra[2,1,9-*def*6,5,10-*d'e'f'*]diisoquinoline-1,3,8,10-tetraone (11): Toluene (6 mL) and 2,9-bis-[2-(hydroxymethyl)-2-octyldecyl]anthra[2,1,9-*def*6,5,10-*d'e'f'*]diisoquinoline-1,3,8,10-tetraone [24] (40 mg, 0.040 mmol) were stirred under argon atmosphere, treated with triethylamine (88 mg, 0.85 mmol) and methacryloylchloride (89 mg, 0.85 mmol), stirred at 20°C for 3 d, evaporated in vacuo, purified by column separation (silica gel, chloroform/acetone 100:1) dissolved in a minimal amount of chloroform, precipitated with methanol and dried at 110°C for 16 h. Yield 26 mg (57%), red solid, m.p. 152°C. R_f (silica gel, chloroform/acetone 100:1): 0.42. IR (ATR): $\tilde{\nu} = 2954$ (m), 2923 (s), 2853 (m), 1699 (s), 1658 (s), 1616 (w), 1594 (s), 1578 (m), 1507 (w), 1456 (m), 1437 (m), 1404 (m), 1373 (m), 1336 (s), 1295 (m), 1250 (m), 1217 (w), 1166 (s), 1126 (m), 1012 (m), 986 (m), 935 (m), 890 (w), 857 (m), 834 (w), 810 (s), 796 (m), 748 (s), 721 (m), 673 cm⁻¹ (w). ¹H NMR (CDCl₃/TMS, 600 MHz): $\delta = 0.86$ (t, $^3J_{H,H} = 7.0$ Hz, 12 H, 6 × CH₃), 1.19 - 1.50 (m, 56 H, 28 × CH₂), 1.68 (s, 6 H, 2 × CH₃), 4.06 (s, 4 H, 2 × CH₂-N), 4.31 (s, 4 H, 2 × CH₂-OH), 5.16 - 5.19 (m, 1 H, C = CH), 5.79 (s, 1 H, C = CH), 8.36 (d, $^3J_{H,H} = 7.1$ Hz, 4 H, 2 × CH_{per}), 8.47 ppm (d, $^3J_{H,H} = 7.6$ Hz, 4 H, 2 × CH_{per}). ¹³C NMR (CDCl₃/TMS, 150 MHz): $\delta = 167.20, 164.04, 136.48, 134.24, 131.40, 129.07, 126.07, 124.85, 123.34, 122.96, 69.17, 45.26, 41.79, 33.93, 32.02, 30.74, 29.67, 29.45, 23.28, 22.81, 18.23, 14.25$ ppm. UV/Vis (CHCl₃): λ_{max} (ϵ) = 458 (17,100), 489 (50,900), 526 nm (85,900). Fluorescence (CHCl₃, $\lambda_{exc} = 490$ nm): λ_{max} (I_{rel}): 534 (1.0), 575 (0.50), 623 nm (0.12). Fluorescence quantum yield (CHCl₃, λ_{exc} =

490 nm, $E_{490\text{nm}/1\text{cm}} = 0.0544$, reference: S-13 with $\Phi = 1.00$): $\Phi = 0.85$. MS (DEI+, 70 eV): m/z (%) = 1091.4 (73) [MH^+], 1090.4 (100) [M^+], 1004.6 (11) [$M^+ - C_{66}H_{88}N_2O_6$], 741.4 (33) [$M^+ - C_{47}H_{53}N_2O_6$], 404.1 (50) [$M^+ - C_{25}H_{12}O_4N_2$]. MS (FAB+/70 eV): m/z = 1091.4 [MH^+], 1006.3 [$M^+ - C_{66}H_{90}N_2O_6$], 741.9 [$M^+ - C_{47}H_{53}N_2O_6$]. MS (FAB-/70 eV): m/z = 1090.1 [M]. HRMS ($C_{70}H_{94}N_2O_8$): Calcd. m/z : 1090.7010, found m/z : 1090.7013, $\Delta = 0.0003$ mmu. $C_{70}H_{94}N_2O_8$ (1090.7): Calcd. C 77.03, H 8.68, N 2.57; found C 77.03, H 8.75, N 2.54.

ONP by RAFT co-polymerisation of polymerizable labels with styrene and methylmethacrylate, respectively; general procedure: The polymerizable labels **1** until **9** were dissolved in freshly distilled styrene and methylmethacrylate, respectively, treated with 2,2'-azo-bis-isobutyronitrile (AIBN) and then with *S*-cyanomethyl-*S*-dodecylcarbonotrithioate (**10**) and 2-cyanopropan-2-yl-dodecylcarbonotrithioate, respectively, stirred under argon atmosphere for 5 min, stirred a definite time at 70°C for polymerisation (delay for heating about 12 until 15 min), quenched by the addition of the quantity of a micro spatulum of hydroquinone, treated with a small amount of toluene (max. 5 mL), precipitated with methanol, repeatedly dissolved in toluene and precipitated with methanol until neither a coloration nor fluorescence (365 nm fluorescent lamp) could be detected of the liquid phase and dried in air at 80°C; see **Table 1** and **Table 2**.

ONP-doped polymers by means of polymerisation: 50 ... 100 ppm ONP and AIBN (1.5 mg, 0.009 mmol) were stirred with the monomer (9 g) styrene and methylmethacrylate, respectively, until homogeneous, treated with further monomer (1 g), stirred for 15 min, treated with AIBN (1.5 mg, 0.009 mmol), polymerised at 70°C for 1.5 h and hardened at 47°C for 3 d. The fluorescence of the ONP could be detected with optical excitation at 490 nm and corresponds to the fluorescence of the isolated ONP.

ONP-doped polymers by means of incorporation: 50 ... 100 ppm ONP (until 300 ppm ONP for **15** and **16**) and technical Delrin (polyoxomethylene, 3 g) were treated with chloroform (1 mL), homogenized by stirring, allowed to evaporate in air, melt by means of a heat gun at about 300°C with stirring and kneading for 3 min and shock cooled in liquid nitrogen. The fluorescence of ONP could be detected with optical excitation at 490 nm.

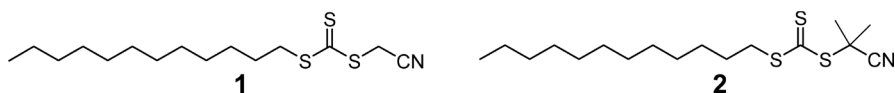
Degradation of ONP-doped Delrin: Doped Delrin was refluxed with concentrated hydrochloric acid (bath 120°C) until dissolution (15 min until 1 h depending on technical processing), allowed to cool, extracted with chloroform and characterized by UV/Vis spectroscopy. Absorption and fluorescence spectra of the applied chromophores were obtained.

3. Results and Discussion

3.1. RAFT Polymerisation

We have applied the radical-induced RAFT polymerisation [13] (Reversible Addition Fragmentation chain Transfer) to styrene, where the chain propagation

was controlled by the concentration of added RAFT reagent **1** [18].



The reversible addition of radicals to the trithiocarbonate structure of **1** causes a low stationary concentration of free radicals both with uniform conditions for

Table 1. Synthesis of styrene-based ONP according to the general procedure: **12** [absorption λ_{max} (E_{rel}) = 527 (1.00), 490 (0.61), 459 nm (0.24); fluorescence λ_{max} (I_{rel}) = 535 (1.00), 577 (0.51), 626 nm (0.12)], **13** [absorption λ_{max} = 589 nm; fluorescence λ_{max} = 600 nm]; **14** [absorption λ_{max} (E_{rel}) = 654 (1.00), 600 (0.64), 555 nm (0.32); fluorescence λ_{max} (I_{rel}) = 673 (1.00), 736 nm (0.46)], **15** [absorption λ_{max} (E_{rel}) = 479 (0.15), 439 (0.54), 417 (0.41), 367 nm (1.00); fluorescence λ_{max} (I_{rel}) = 500 (1.00), 523 nm (0.84)], **16** [absorption λ_{max} (E_{rel}) = 467 (1.00), 437 (0.66), 410 (0.33), 377 nm (0.57); fluorescence λ_{max} (I_{rel}) = 467 (1.00), 508 nm (0.97)]. Fluorescence quantum yield Φ . Fluorescence excitation at 490 nm.

ONP	Label	m_{label} [mg]	m_{styrene} [g]	$m_{(10)}$ [mg]	m_{AIBN} [mg]	t [h]	Yield [g]	$m_{\text{dye}}/m_{\text{ONP}}$ [mg/g]	Φ
12a	3	5	10	25	15	24	3.43	0.547	95%
12b	3	5	10	50	15	24	1.53	0.484	79%
12c	3	5	10	100	15	24	2.15	0.462	91%
12d	3	5	10	150	15	24	1.22	0.427	86%
12e	3	5	10	150	15	24	2.43	0.333	92%
12f	3	5	10	200	15	24	1.87	0.510	93%
12g	3	5	10	400	15	24	0.10	0.930	83%
12h	3	3.5	5.0	50	7.5	24	1.85	1.25	59%
12i	3	5.0	5.0	50	7.5	24	2.30	0.990	82%
12j	3	10	5.0	50	7.5	24	1.52	2.67	70%
12k	3	15	5.0	50	7.5	24	0.51	8.11	75%
12l	3	20	5.0	50	7.5	24	0.49	9.72	76%
13a	4a/b	5	10	50	15	24	1.43	0.57	$\approx 100\%$
13b	4a/b	5	10	100	15	24	1.23	0.64	$\approx 100\%$
13c	4a/b	5	10	150	15	24	2.65	0.47	$\approx 100\%$
13d	4a/b	5	10	200	15	24	0.64	0.71	96%
13e	4a/b	5	10	400	15	24	0.63	0.84	$\approx 100\%$
14	5	2.5	5.0	100	7.5	24	0.98	0.12	66%
15	6	1.0	2.0	50	3.75	24	0.13	2.97	3%
16a	7	2.5	5.0	25	7.5	24	1.34	2.3	0.2%
16b	7	2.5	5.0	50	7.5	24	1.21	4.8	0.3%
16c	7	2.5	5.0	75	7.5	24	0.20	4.8	0.2%
16d	7	2.5	5.0	100	7.5	24	0.10	3.5	0.2%

Table 2. Synthesis of methylmethacrylate-based ONP (MMA) according to the general procedure: **17a** [absorption $\lambda_{\max}(E_{\text{rel}}) = 527$ (1.00), 490 (0.63), 459 nm (0.23); fluorescence $\lambda_{\max}(I_{\text{rel}}) = 535$ (1.00), 577 (0.51), 625 nm (0.13)], **18a** [absorption $\lambda_{\max}(E_{\text{rel}}) = 527$ (1.00), 490 (0.63), 459 nm (0.25); fluorescence $\lambda_{\max}(I_{\text{rel}}) = 535$ (1.00), 577 (0.51), 625 nm (0.13)]; **19** [absorption $\lambda_{\max}(E_{\text{rel}}) = 527$ (1.00), 491 (0.63), 459 nm (0.25); fluorescence $\lambda_{\max}(I_{\text{rel}}) = 535$ (1.00), 576 (0.59), 625 nm (0.12)], **20** [absorption $\lambda_{\max}(E_{\text{rel}}) = 526$ (1.00), 490 (0.63), 459 nm (0.25); fluorescence $\lambda_{\max}(I_{\text{rel}}) = 534$ (1.00), 576 (0.50), 625 nm (0.12)]. Fluorescence quantum yield Φ . Fluorescence excitation at 490 nm.

ONP	Label	m_{label} [mg]	m_{styrene} [g]	$m_{(10)}$ [mg]	m_{AIBN} [mg]	t [h]	Yield [g]	$m_{\text{dye}}/m_{\text{ONP}}$ [mg/g]	Φ
17a	8	5.0	2.0	10	3.0	24	0.35	0.357	96%
17b	8	5.0	2.0	10	3.0	24	0.33	0.252	99%
17c	8	2.5	2.0	10	3.0	24	0.31	0.244	87%
17d	8	2.5	2.0	5	3.0	24	0.30	0.142	80%
17e	8	2.5	2.0	20	3.0	24	0.25	0.185	51%
17f	8	5.0	2.0	10	3.0	3	0.18	0.408	93%
17g	8	2.5	2.0	10	3.0	3	0.12	0.276	78%
17h	8	2.5	2.0	5	3.0	3	0.09	0.322	89%
17i	8	5.0	2.0	10	3.0	1	0.08	0.620	71%
17j	8	2.5	2.0	5	3.0	3	0.07	0.194	81%
18a	9	5.0	2.0	10	3.0	3	0.14	0.794	75%
18b	9	2.5	2.0	5	3.0	3	0.35	0.310	76%
18c	9	2.5	2.0	10	3.0	3	0.44	0.656	≈100%
18d	9	2.5	2.0	5	3.0	1	0.10	0.203	≈100%
19a	10	5.0	2.0	10	3.0	3	0.11	0.832	88%
19b	10	2.5	2.0	10	3.0	3	0.04	0.210	83%
19c	10	2.5	2.0	10	3.0	1	0.40	0.827	82%
19d	10	2.5	2.0	5	3.0	1	0.03	1.140	76%
20	11	2.5	2.0	5	3.0	3	0.08	3.28	82%

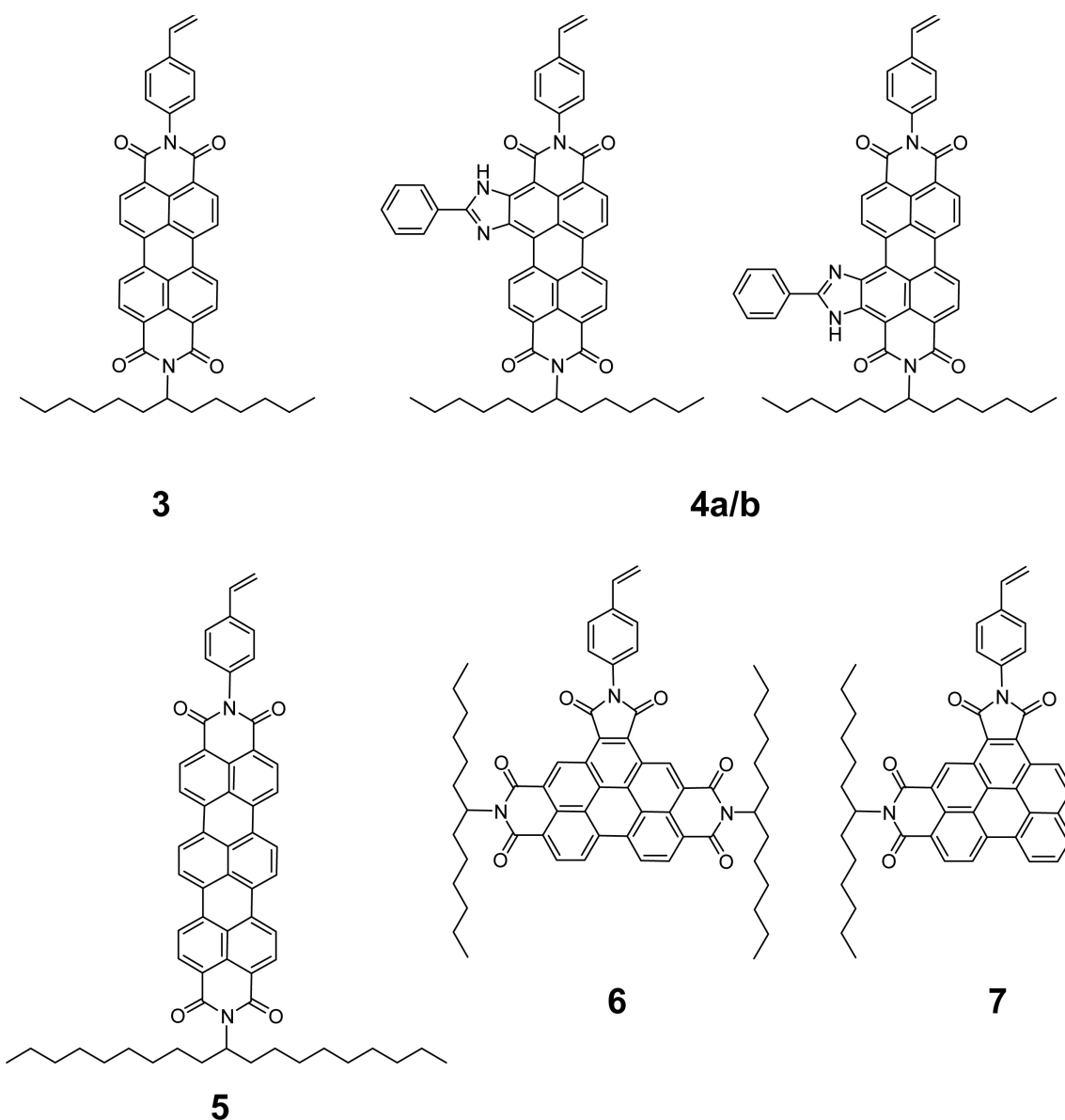
the chain propagation and a suppression of the bimolecular termination by combination and disproportionation reactions [19] [20] [21]. The consequence is a narrow distribution of the molecular weight and a targeted nearly uniform size of the thus formed polymeric particles, respectively. As an alternative, we polymerised MMA (methyl methacrylate) under RAFT conditions where we applied the reagent [14] **2** because of more similarity with MMA and the polymeric PMMA than **1**. The monomeric styrene was copolymerized with vinylphenyl groups attached to chromophores for the introduction of fluorescence into the ONP. Alternatively, methacyclic esters of chromophores were copolymerised with MMA.

3.2. Synthesis of Fluorescent Labels

Perylenes [15] [16] were applied as basic structures of fluorescent chromophores

because of their chemical and photochemical stability and high fluorescence quantum yields. Their inherently low solubility was overcome by the attachment of long-chain secondary alkyl groups (swallow-tail substituents) such as the 1-hexylheptyl group.

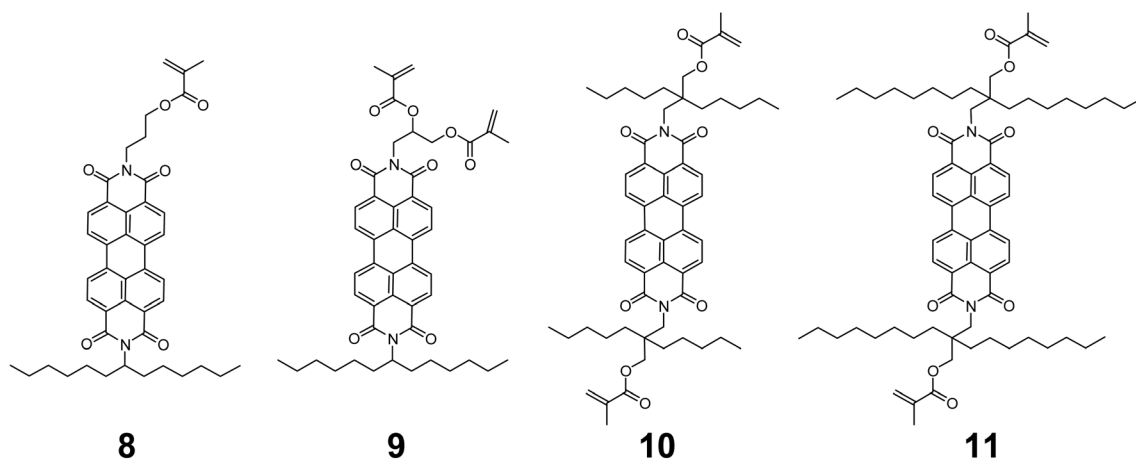
Vinylphenyl-modified perylenes were targeted for co-polymerisation with styrene. Thus, we condensed the corresponding anhydride function with 4-aminostyrene to obtain **3** [17] (see **Scheme 1**). For the more bathochromic spectral region in the UV/Vis the aromatic core of **3** was laterally extended by a phenylimidazolo group [11]. Thus, the corresponding *N,N*-bis-1-hexylheptylbiscarboximide was partially hydrolysed under rough alkaline conditions to end-up in a difficult separable mixture of regio isomeric anhydrides-carboximides that was directly condensed with 4-aminostyrene in the same manner as described for **3** to obtain



Scheme 1. Synthesis of fluorescent labels with vinyl groups.

the mixture **4a/b**. This mixture could not be separated on a preparative scale; however, the UV/Vis spectral properties of **4a** and **4b** are so similar that a separation is not necessary for practical applications (TLC separation, nearly uniform UV/Vis spectra). For covering the even more bathochromic spectral region terrylenebiscarboximides were applied meaning a naphthalene-core-prolonged perylenebiscarboximide. Synthesis started similarly to **4a/b** with a terrylene bis-carboximide [18] with two even more effectively solubilising 1-nonyldecyl substituents, hydrolysing to give the corresponding anhydridecarboximide and its condensation with 4-aminostyrene to obtain **5**. For the more hypsochromic spectral region perylenebiscarboximide with two solubilising 1-hexylheptyl substituents was core-modified by means of a Diels-Alder-Clar reaction with maleic anhydride leading in a five-membered ring anhydride [25] that was condensed with 4-aminostyrene to obtain the benzoperylene-derived label **6**. Furthermore, benzoperyleneanhydride-carboximide [22] was allowed to condense with 4-aminostyrene in the same manner to obtain the benzoperylenedicarboximide **7**.

We prepared methacrylic esters of chromophores for more similarity in the co-polymerisation with MMA. Thus, the well-accessible perylenetetracarboxylic-3,4-anhydride-9-carboxylicacid-10-potassium salt [26] [27] was condensed with 3-hydroxypropylamine, then with 1-hexylheptylamine and allowed to react with methacryloylchloride to obtain **8** (see Scheme 2). Two methacroylester groups were attached in **9** for cross linking. Thus, the perylene anhydride-carboximide with the solubilising 1-hexylheptyl substituent attached to the nitrogen atom was condensed [23] with aminodihydroxypropane and allowed to react with methacryloylchloride for the preparation of **9** where the chromophore remains attached to the side chain of the polymer. For a cross-linking across the chromophore perylenetetracarboxylic bisanhydride was condensed [24] with 2-aminomethyl-2-pentylheptyl-1-ol where the solubilising effect was brought-about by the geminal alkyl groups. Further reaction with methacryloyl chloride gave **10**. The solubilising effect of the geminal alkyl groups could be further increased by means of a prolongation of the alkyl groups to obtain **11** in the same manner as described



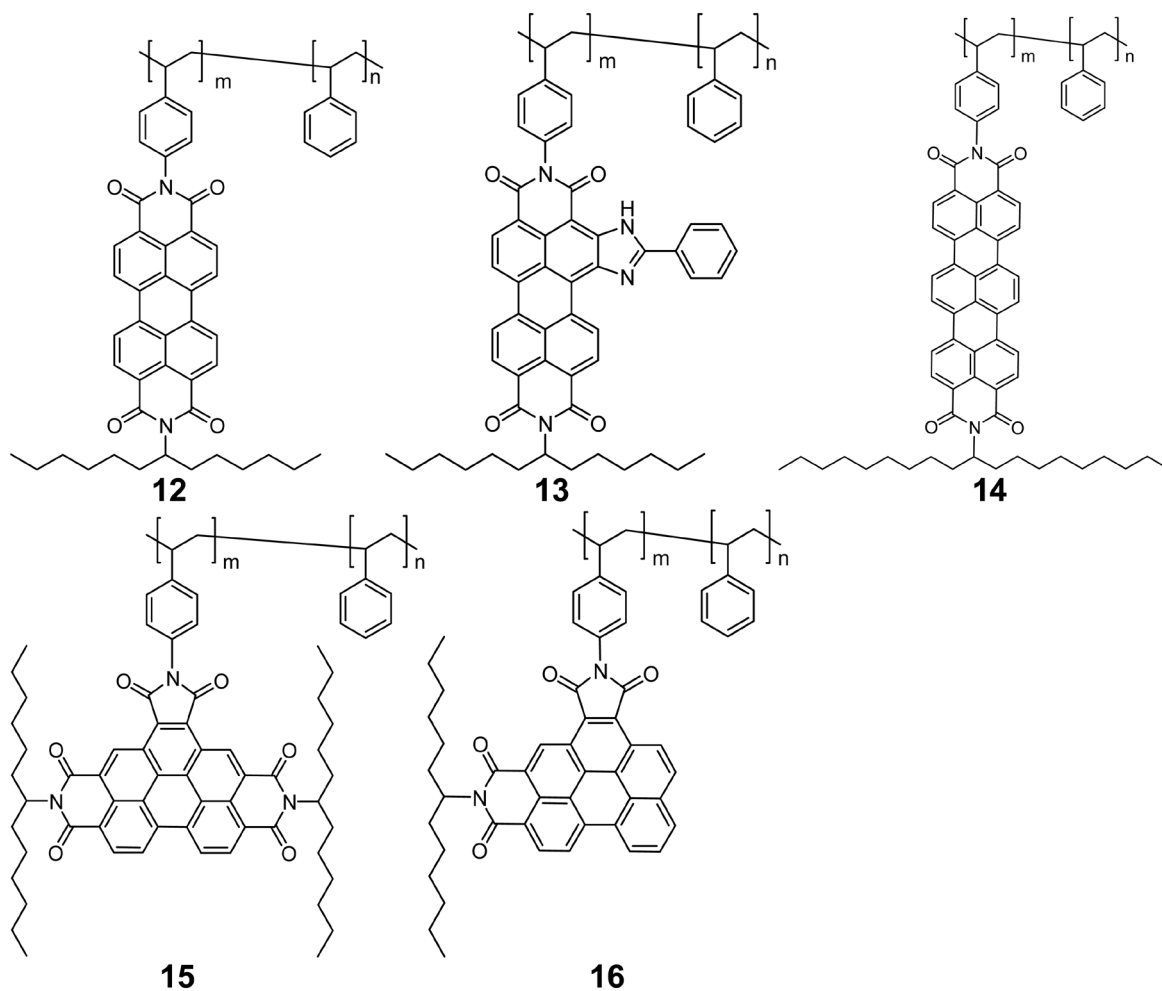
Scheme 2. Synthesis of fluorescent labels with methacrylic ester groups.

above for **10**.

3.3. Fluorescent Organo-Nano Particles (ONP)

Radical RAFT polymerisation (Reversible Addition-Fragmentation chain Transfer) mediated and over-all controlled by **1** was applied to a mixture of styrene and **3** until **7** for the preparation of ONP **12** until **16** as co-polymers (see **Scheme 3**). The reactions proceeded smoothly without problems concerning the Trommsdoff effect. A comparably narrow distribution in molecular weight of **12** was obtained with polydispersities *PD* as low as about 1.1 (1.04 until 1.19); see **12a** until **12g** in **Table 1** and **Table 3**.

The molecular weights M_n of **12** decrease with increasing concentrations of **1** from 23,300 to 3300 (**12a** until **12g**) and the size decreases from 66 nm to 7 nm where the smaller nano particles seem to be more compact presumably because of the local influence of the chromophore. An increase of the concentration of labelling agent **3** (**12h** until **12l**) decreases also the molecular weight, however, not as pronounced as with increasing concentrations of **1**. An aggregation of **3** at higher concentrations is indicated by a colour deepening from orange to red and



Scheme 3. Fluorescent organonanoparticles (ONP).

Table 3. ONP by the copolymerisation of **3** until **7** and styrene under RAFT condition mediated by **1**; M_n and M_w by GPC (UV detector, acetonitrile, calibration with polystyrene). Size by DLS.

ONP	Label	M_n [g/mol]	M_w [g/mol]	PD	Size [nm]
12a	3	23,300	26,800	1.15	44
12b	3	27,300	31,300	1.15	63
12c	3	14,300	15,500	1.07	22
12d	3	11,100	11,900	1.08	13
12e	3	9900	10,300	1.04	14
12f	3	6200	6500	1.04	7
12g	3	3300	3600	1.07	7
12h	3	20,700	23,500	1.13	23
12i	3	21,200	25,300	1.19	26
12j	3	13,900	15,800	1.14	16
12k	3	6800	7400	1.09	10
12l	3	7900	9200	1.16	19
13a	4a/b	14,200	15,500	1.09	19
13b	4a/b	12,700	13,700	1.08	10
13c	4a/b	9960	10,600	1.07	9
13d	4a/b	5600	5900	1.06	10
13e	4a/b	3500	3700	1.07	9
14	5	14,800	16,400	1.11	75 ^a
15	6	7300	8100	1.08	33
16a	7	22,900	28,500	1.24	21
16b	7	28,000	36,600	1.31	41
16c	7	18,100	21,700	1.19	26
16d	7	29,700	37,900	1.28	36

a. Interference of the signal processing with fluorescence.

is made responsible for the lowering of the size by impeding the polymerization. Finally, the size of the nano particles can be controlled with **1** in the same manner as with the monomers of co-polymerisation of styrene such as for **4a/b** (**13a** until **13d**) and **7** (**16a** until **16d**).

A further type of ONP was prepared on the basis of PMMA (polymethyl methacrylate) where methyl methacrylate was co-polymerised under RAFT condition. Markers **8** until **11** were applied and the reaction was controlled by means of **2**; see **Table 2** and **Table 4**. The scope of reproducibility of the synthesis is indicated by **17a** and **17b** where the decrease of the concentration of marker (**17c**) causes as well larger particles as an decrease of the concentration of **2** (**17d**); this corresponds completely to **12**. Comparably large ONP were obtained with a

Table 4. ONP by the copolymerisation of **8** until **11** and methyl methacrylate under RAFT condition controlled by **2**; M_n and M_w by GPC. Size by DLS.

ONP	Label	M_n [g/mol]	M_w [g/mol]	PD	Size [nm]
17a	8	61,600	80,700	1.31	82
17b	8	53,300	66,800	1.26	41
17c	8	52,100	98,800	1.32	161
17d	8	82,300	112,300	1.37	233
17e	8	25,600	31,300	1.22	14
17f	8	29,200	35,300	1.21	20
17g	8	21,700	25,200	1.16	14
17h	8	30,600	37,300	1.22	18
17i	8	19,400	22,600	1.17	11
17j	8	30,600	37,400	1.22	30
18a	9	21,700	26,500	1.17	11
18b	9	42,100	57,500	1.22	32
18c	9	57,100	76,000	1.33	34
18d	9	22,300	28,200	1.26	16
19a	10	22,900	28,500	1.24	21
19b	10	28000	36,600	1.31	41
19c	10	18,100	21,700	1.19	26
19d	10	29,700	37,900	1.28	36
20	11	61,600	80,700	1.31	76

reaction time of 24 h (**17a** until **17e**). The shortening of the reaction time to 3 h (**17f** until **17h**) and even to 1 h (**17i**) decreases the size of the ONP appreciably until 11 nm. The lowering of the concentration of the RAFT reagent **2** (**17g**, **17h** and **17j**) causes an increase of the molecular weight and the size of particles, respectively. The same influence was found for **1** and polystyrene even for short reaction times (**17i**).

The bis-ester **9** can be expected to act as a cross-linker where the chromophore is situated at the side chain (**18a** until **18d**). The concentration of the RAFT reagent **2** influences the size not as pronounced as for **8** (**18b** and **18c**); the reaction time and the concentration of the cross linker **9** (**18a** and **18c**) are more important (**18b** and **18d**). An aggregation of the chromophore constraining the growths of the chains is made therefore responsible; the latter is indicated by a colour deepening of the ONP from orange to red with increasing concentration of the marker. Surprisingly, it seems of minor importance whether the chromophore is placed in the cross linking position or not (**19a** until **19d**). A lowering of the concentration of the cross linker increases the size of the particles (**19a** and **19b**) where the reaction time is more important (**19b** and **19c**) than the concentration of **2** (**19c** and **19d**). Finally, an increase of the chain length of the

solubilising groups causes the formation of larger ONP (**18b** and **20**). The properties of cross-linked and linear ONP seem to be similar, however, the cross-linking causes of the particles to dissolve more slowly in organic solvents.

A comparably low molecular weight was found for the nano particles **12g** by means of GPC and could be verified with MALDI as is shown in **Figure 1**. The pattern of peaks corresponds to the mass differences of units of styrene. A uniform size can be seen in **Figure 2**.

The ONP exhibit a comparably narrow distribution in size determined by means of dynamic light scattering (DLS); this corresponds to their low values of the polydispersity *PD* (see **Table 1** and **Table 2**). The very small particles **17i** exhibit a broader distribution in size; this may be caused by the influence of the larger share of the chromophore. The distribution in size of the typical samples **18a** until **18d** is shown in **Figure 3**.

The thermal stability of ONP was tested by means of thermogravimetry (TGA) and reported for the typical samples **12a** and **17a** in **Figure 4**. The particles were completely stable until 200°C. A loss of mass between 10 and 13% proceeds slightly above 200°C and is attributed to a loss [28] of the terminal trithiocarbonate group. On the other hand, this does not affect the function of the fluorescent nano particles being thermally stable until more than 300°C. Thus, the ONP can be applied under conditions of the processing of technical polymers.

The perylene-derived chromophores remain nearly unaffected by the incorporation into ONP as is shown in **Figure 5** where both the structured absorption

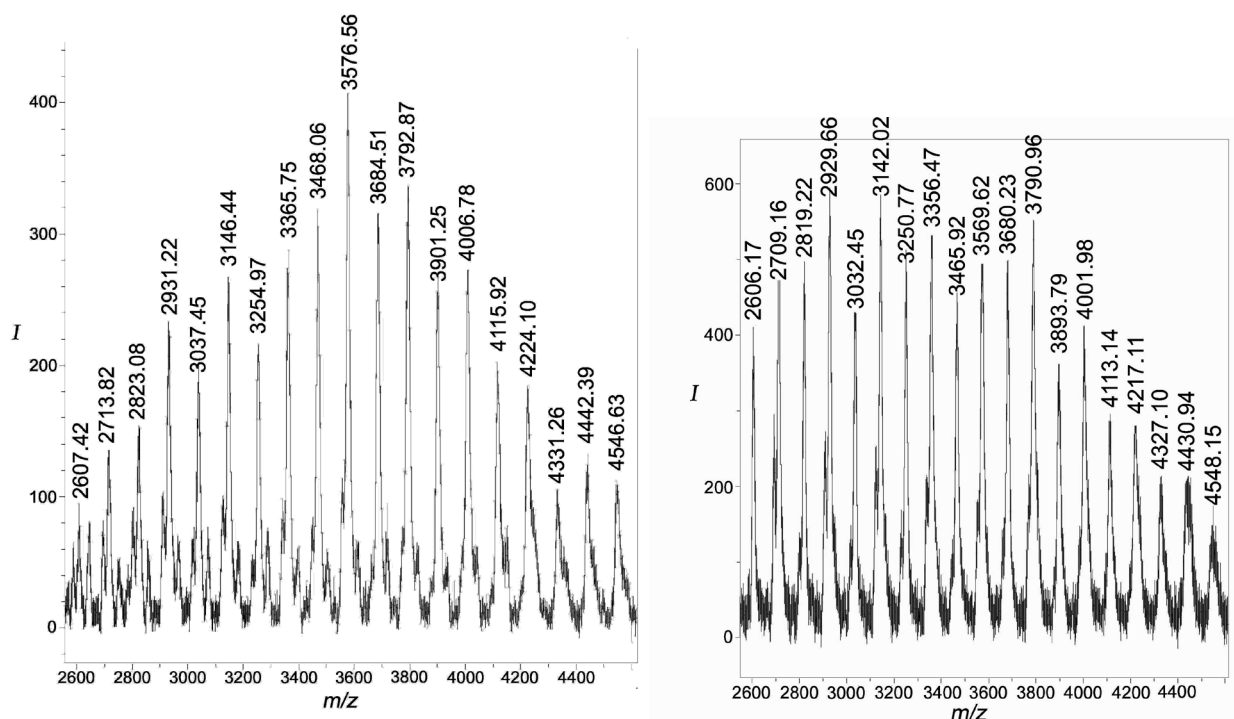


Figure 1. Segments of the MALDI spectra of the styrene-based ONP **12g** in reflection mode. Left: Positive ionisation. Right: Negative ionisation (matrix IAA + AgTFA in THF).

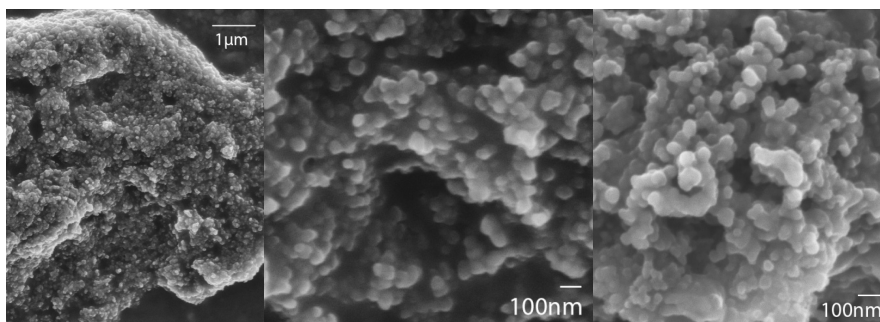


Figure 2. SEM representations of ONP **12b** (left and middle) and **12d** (right).

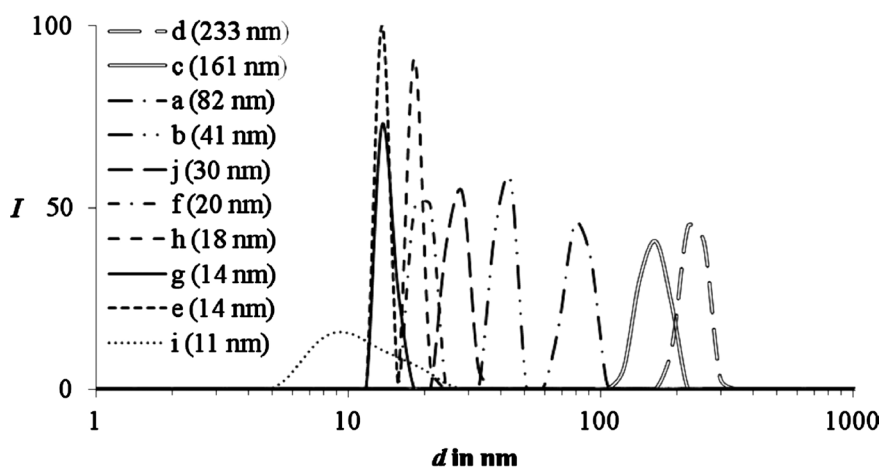


Figure 3. Size distribution d in nm of the ONP **17a** until **17j** by means of DLS.

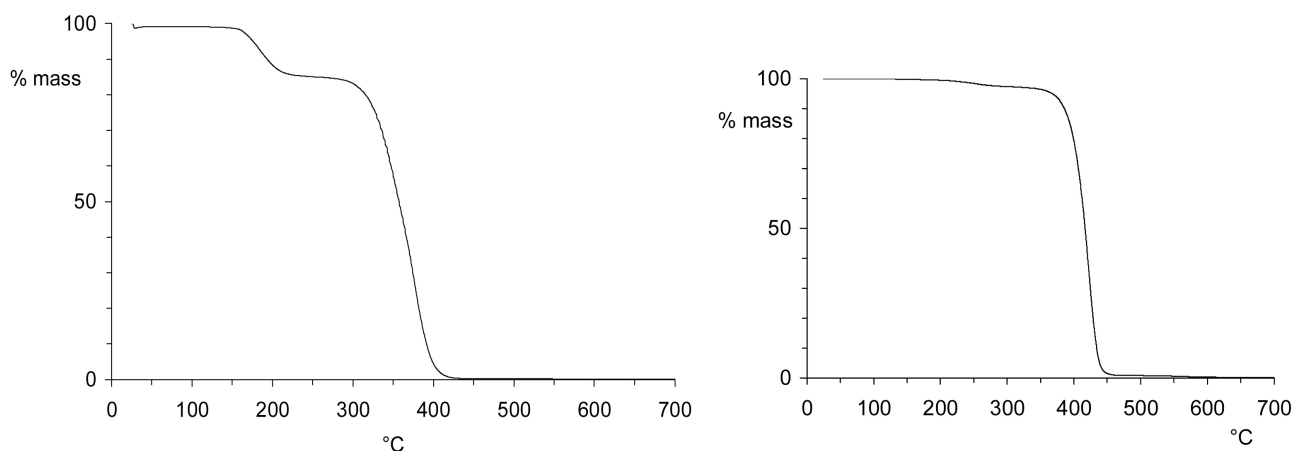


Figure 4. Thermo gravimetry (TGA) of the ONP **12a** (left) and **17a**.

and fluorescence of ONP **12** are very similar to the spectra of the chromophore in homogeneous solution; for comparison see, for example ref. [15] [16]. The particles are highly fluorescent, see **Table 1** and **Table 2**, and the light emission of ONP **12** until **16** covers the most of the visible region as is shown in **Figure 6**.

The ONP can be incorporated into polymers for applications such as fluorescent labelling. The more styrene-similar ONP **12** until **16** were spread in monomeric styrene and the more methacrylate-like ONP **17** until **20** preferentially in

methyl methacrylate, respectively, and polymerised with a free radical-generating initiator (the Trommsdorff effect could be avoided by a slow processing). Highly transparent materials were obtained where the PMMA (polymethyl methacrylate) is even more clear than the PS (polystyrene). The fluorescent spectra of the doped PS containing the ONP **12** until **15** are reported in **Figure 6**, left. POM (polyoxomethylene) was doped by the treatment of dissolved ONP, rapidly melt with stirring and chilling with liquid nitrogen. The fluorescence spectrum of the

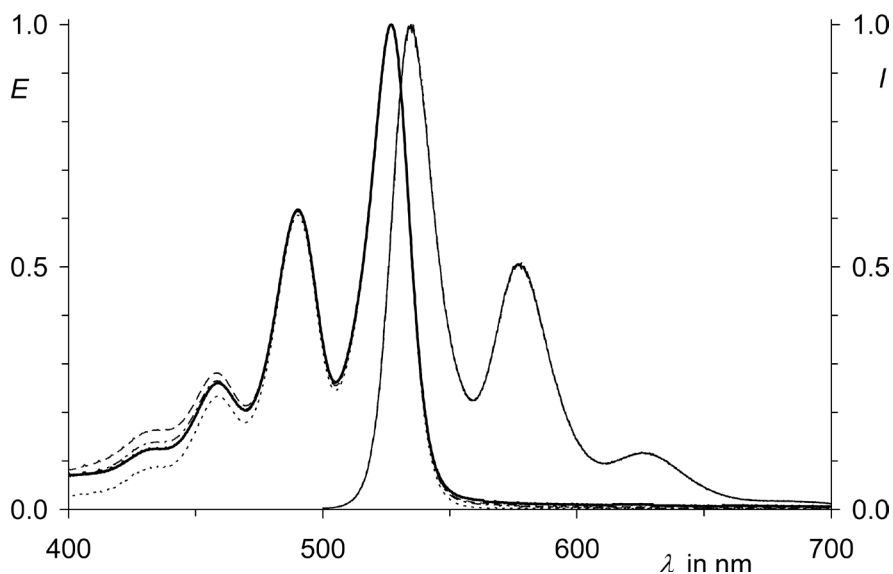


Figure 5. The very similar UV/Vis absorption (left, left abscissa, maxima at 526, 489 and 457 nm) and fluorescent spectra (right, right abscissa, nearly congruent spectra, maxima at 535, 578 and 627 nm, optical excitation at 589 nm) of ONP **12a** (solid line), **12b** (dotted) **12c** (dashed) and **12d** dotted dashed in chloroform.

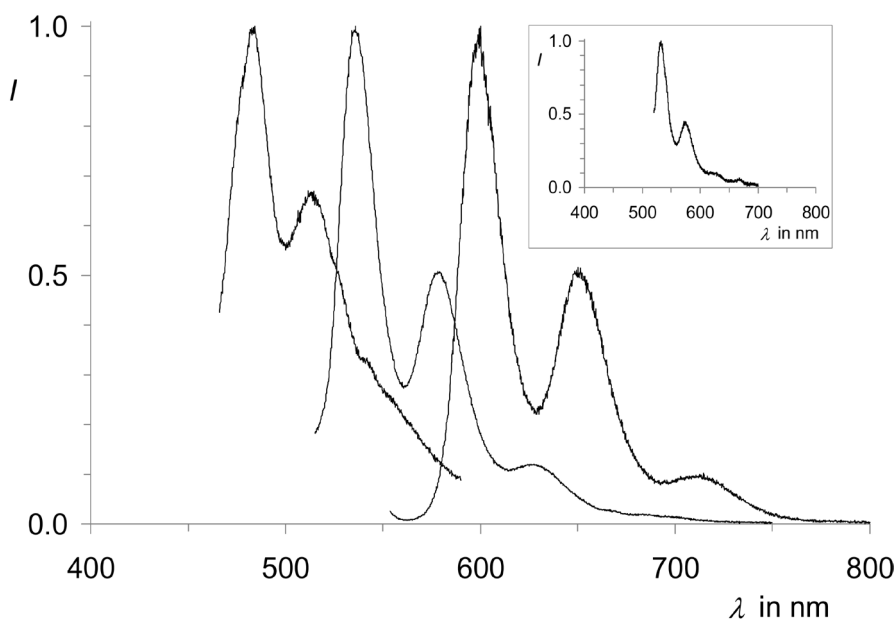


Figure 6. Left from left to right: The fluorescence spectra of the ONP **15**, **12** and **13** in polystyrene. Inset: ONP **12** in technical POM (polyoxomethylene, Delrin®).

ONP **12**-doped POM is reported in **Figure 6**, right. The fluorescence spectra of the doped polymers are identical with the spectra of dissolved ONP. A doping as low as 5 ppm ONP can be easily detected with routine fluorescence spectrometers. The doping of PMMA plates with such low concentrations render the material colorless, however, slight fluorescence can be even visually seen at the edges because of the light amplification caused by the effect known from the fluorescence planar concentrator [29]. The fluorescence signal increases with doping linearly until 100 ppm. At even higher concentrations the increase is damped attributed to the aggregation of ONP. Similar results were obtained with the polymers Luran[®] (polystyrene/polyacrylonitrile copolymer) and Ultramid[®] (polyamide compound material).

The doping of polymers exhibit a high light fastness; this is demonstrated with a doped PMMA plate in **Figure 7** where no photo degradation of the fluorescent signal could be observed under the influence of direct sunlight. Measurements scatter in the same way as for a sample stored in the dark. No fading of fluorescence was visually observed for ONP-doped PMMA plates exposed to ambient light over a period of more than two years. As a consequence, the reported fluorescent ONP are suitable fluorescent marker [30] for polymers in practical applications where their nano dimensions are of special advantage because restricting migrations.

The ONPs can be easily handled as stable powders at room temperature for months; the long-term stability and possibilities of degradation, respectively, were studied by exposure to air for a period of three years. Appearance and fluorescence remained unaltered, however, GPC measurements indicated some degradation with lowering the number average of the molecular weight M_n .

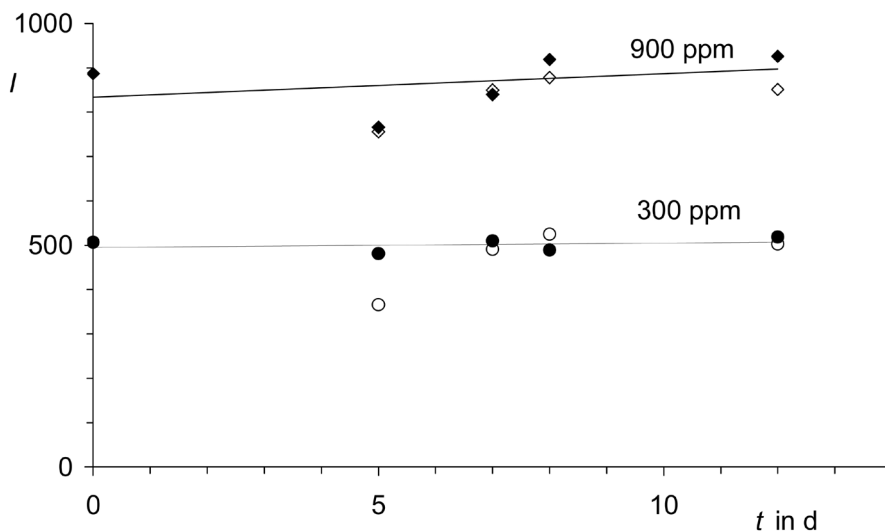


Figure 7. Stability test of ONP **12b** in a PMMA plate (5 mm). Abscissa: Time of irradiation with direct sunlight (Munich, May 2015). Ordinate: Fluorescence intensity I in arbitrary units of the spectrometer. Circles: doping with 300 ppm ONP, diamonds doping with 900 ppm ONP. Filled symbols: Irradiated sample. Open symbols: references stored in the dark.

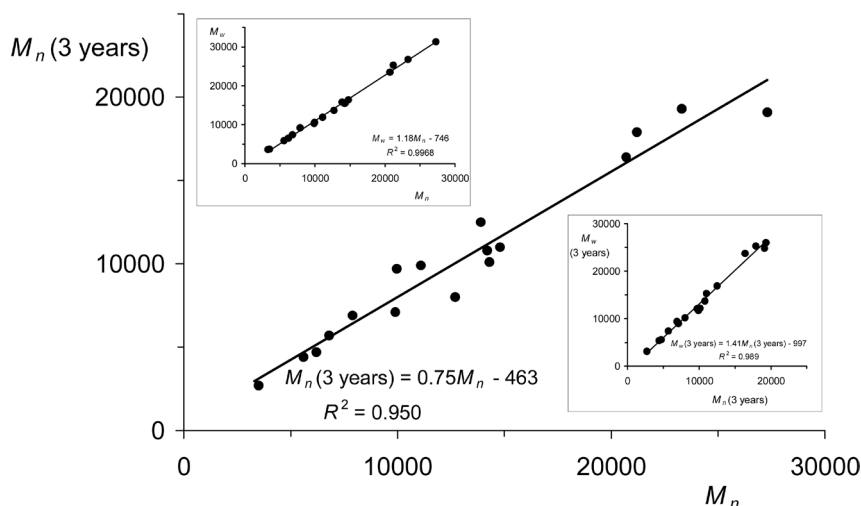


Figure 8. Aging of ONP: The number average of the molecular weights M_n of ONPs (see Table 5) and the influence of the exposition to air at room temperature after a period of three years [M_n (3 years)]; the slope < 1 indicates stronger alterations of larger particles. Inset upper left: Linearity between M_n and M_w for ONPs; the slope slightly larger than 1 indicates a higher uniformity of smaller particles. Inset lower left: Linearity between M_n (3 years) and M_w (3 years) for ONPs after an exposition to air after a period of three years (3 years); the slope slightly higher than the slope of the upper left diagram indicates a stronger alteration of the larger ONPs by ageing.

Table 5. Aging of ONP: The number average of the molecular weights M_n , the weight average of the molecular weight M_w of ONP and changes after the exposure to air at room temperature for a period of three years [M_n (3 years), M_w (3 years) and PD (3 years)].

ONP	M_n [g/mol]	M_w [g/mol]	PD	M_n (3 years) [g/mol]	M_w (3 years) [g/mol]	PD (3 years)
12a	23,300	26,800	1.15	19,300	26,000	1.35
12b	27,300	31,300	1.15	19,100	24,800	1.30
12c	14,300	15,500	1.08	10,100	12,200	1.21
12d	11,100	11,900	1.07	9900	11,700	1.18
12e	9900	10,300	1.04	7100	9000	1.27
12f	6200	6500	1.05	4700	5600	1.19
12g	3300	3600	1.09			
12h	20,700	23,500	1.14	16,400	23,700	1.45
12i	21,200	25,300	1.19	17,900	25,300	1.41
12j	13,900	15,800	1.14	12,500	16,900	1.35
12k	6800	7400	1.09	5700	7400	1.30
12l	7900	9200	1.16	6900	9400	1.36
13a	14,200	15,500	1.09	10,800	13,700	1.27
13b	12,700	13,700	1.08	8000	10,200	1.28
13c	9960	10,600	1.06	9700	12,100	1.25
13d	5600	5900	1.05	4400	5400	1.23
13e	3500	3700	1.06	2700	3100	1.15
14	14,800	16,400	1.11	11,000	15,300	1.39
15	7300	8100	1.11			
16a	22,900	28,500	1.24			
16b	28,000	36,600	1.31			
16c	18,100	21,700	1.20			
16d	29,700	37,900	1.28			

preferentially for larger ONPs (slope < 1 in **Figure 8**) and an increase of the polydispersity *PD* to about 1.4; see **Table 5** and **Figure 8**. We conclude that the stability of the ONPs is high enough for processing, whereas a slow degradation can be expected in the environment attributed to the very high surface of the particles.

4. Conclusion

Organo-nanoparticles (ONP) with narrow distribution of size can be prepared by RAFT polymerisation where the co-polymerisation with vinyl-substituted chromophores introduces fluorescence as a functionality of such materials. The size of the ONP is controlled both by the concentration of the applied RAFT reagent and the amount of added polymerisable chromophore for co-polymerisation. Small ONP are more compact than larger ones indicated by the relatively smaller size compared with their molecular weight. Adapted perylene-derived chromophores allow the preparation of strongly fluorescent ONP with emission covering the whole visible region. Application of ONP as non-migrating markers of polymers is of interest such as for recycling applications where a binary coding [30] of applied *n* fluorescent marker allows a characteristic labelling of 2^{n-1} materials. Moreover, such marking may be applied for efficient and easily detectable tamper- [31] and forgery-proof [32] optical elements.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

- [1] Holden, P.A., Nisbet, R.M., Lenihan, H.S., Miller, R.J., Cherr, G.N., Schimel, J.P. and Gardea-Torresdey, J.L. (2013) Ecological Nanotoxicology: Integrating Nanomaterial Hazard Considerations across the Subcellular, Population, Community, and Ecosystems Levels. *Accounts of Chemical Research*, **46**, 813-822. <https://doi.org/10.1021/ar300069t>
- [2] Johnston, H., Pojana, G., Zuin, S., Jacobsen, N.R., Moller, P., Loft, S., Semmler-Behnke, M., McGuinness, C., Balharry, D., Marcomini, A., Wallin, H., Kreyling, W., Donaldson, K., Tran, L. and Stone, V. (2013) Engineered Nanomaterial Risk. Lessons Learnt from Completed Nanotoxicology Studies: Potential Solutions to Current and Future Challenges. *Critical Reviews in Toxicology*, **43**, 1-20. <https://doi.org/10.3109/10408444.2012.738187>
- [3] MacPhail, R.C., Grulke, E.A. and Yokel, R.A. (2013) Assessing Nanoparticle Risk Poses Prodigious Challenges. *Nanomedicine and Nanobiotechnology*, **5**, 374-387.
- [4] Warheit, D.B. (2013) How to Measure Hazards/Risks Following Exposures to Nanoscale or Pigment-Grade Titanium Dioxide Particles. *Toxicology Letters*, **220**,

- 193-204. <https://doi.org/10.1016/j.toxlet.2013.04.002>
- [5] Chen, A., Guan, S. and Wen, W. (2017) Polymorphic Organic Nanoparticle and Preparation Method and Application Thereof. Faming Zhuanli Shenqing, CN 107163203 A 20170915.
- [6] Langhals, H. and Pust, T. (2010) Fluorescent Nano Particles in the Aqueous Phase by Polymer Analogous Reaction of Polyvinyl Alcohol. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, **77**, 541-544. <https://doi.org/10.1016/j.saa.2010.06.007>
- [7] Langhals, H., Zgela, D., Schmid, T., Herman, M. and Zwiener, M. (2012) Marking of Polymer Materials with Fluorescent Nanoparticles for Their Automatic Sorting. Ger. Offen. DE 102012014982.4 (July 26, 2012).
- [8] Trommsdorff, E., Kohle, H. and Lagally, P. (1948) Polymerization of Methyl Methacrylates. *Makromolekulare Chemie*, **1**, 169-198. <https://doi.org/10.1002/macp.1948.020010301>
- [9] Schulz, G.V. (1956) Polymerization Kinetics in Highly Concentrated Systems. Kinetics of the Trommsdorff Effect on Methyl Methacrylate. *Zeitschr. Phys. Chem. (Muenchen, Germany)*, **8**, 290-317. https://doi.org/10.1524/zpch.1956.8.5_6.290
- [10] Gerrens, H. (1963) Radical Reactions in Polymerization Processes. *Berichte der Bunsen-Gesellschaft für Physikalische Chemie*, **67**, 741-753.
- [11] Kinzel, S. (2009) Perylenfarbstoffe mit lateraler heterocyclischer Ringerweiterung. PhD Dissertation, Ludwig-Maximilians-Universität, München.
- [12] Demmig, S. and Langhals, H. (1988) Very Soluble and Photostable Perylene Fluorescent Dyes. *Chemische Berichte*, **121**, 225-230. <https://doi.org/10.1002/cber.19881210205>
- [13] Chiefari, J., Chong, Y.K., Ercole, F., Krstina, J., Jeffery, J., Le, T.P.T., Mayadunne, R.T.A., Meijs, G.F., Moad, C.L., Moad, G., Rizzardo, E. and Thang, S.H. (1998) Living Free-Radical Polymerization by Reversible Addition-Fragmentation Chain Transfer: The RAFT Process. *Macromolecules*, **31**, 5559-5562. <https://doi.org/10.1021/ma9804951>
- [14] Chong, Y.K., Moad, G., Rizzardo, E. and Thang, S.H. (2007) Thiocarbonylthio End Group Removal from RAFT-Synthesized Polymers by Radical-Induced Reduction. *Macromolecules*, **40**, 4446-4455. <https://doi.org/10.1021/ma062919u>
- [15] Langhals, H. (2013) Chromophores for Picoscale Optical Computers. In: Sattler, K., Ed., *Fundamentals of Picoscience*, Taylor & Francis Inc. CRC Press Inc., Bosa Roca, 705-727.
- [16] Langhals, H. (2005) Control of the Interactions in Multichromophores: Novel Concepts. Perylene Bisimides as Components for Larger Functional Units. *Helvetica Chimica Acta*, **88**, 1309-1343. <https://doi.org/10.1002/hlca.200590107>
- [17] Langhals, H. and Wetzel, F. (2002) Polymeric Fluorescent Dyes, Their Production and Their Use. Ger. Offen. DE 10233179 (July 22, 2002).
- [18] Langhals, H., Walter, A., Rosenbaum, E. and Johansson, L.B.-Å. (2011) A Versatile Standard for Bathochromic Fluorescence Based on Intramolecular FRET. *Physical Chemistry Chemical Physics*, **13**, 11055-11059. <https://doi.org/10.1039/c1cp20467j>
- [19] Perrier, S. (2008) RAFT Polymerisation, a Versatile Tool for the Production of Nanostructures. *Polymer Preprints*, **49**, 248-249.
- [20] Willcock, H., Lu, A., Hansell, C.F., Chapman, E., Collins, I.R. and O'Reilly, R.K. (2014) One-Pot Synthesis of Responsive Sulfobetaine Nanoparticles by RAFT Polymerisation: The Effect of Branching on the UCST Cloud Point. *Polymer Chemistry*

- try, **5**, 1023-1030. <https://doi.org/10.1039/C3PY00998J>
- [21] Lewis, R.W., Evans, R.A., Malic, N., Saito, K. and Cameron, N.R. (2018) Ultra-Fast Aqueous Polymerisation of Acrylamides by High Power Visible Light Direct Photoactivation RAFT Polymerisation. *Polymer Chemistry*, **9**, 60-68. <https://doi.org/10.1039/C7PY01752A>
- [22] Langhals, H., Böck, B., Schmid, T. and Marchuk, A. (2012) Angular Benzoperylene-tetracarboxylic Bisimides. *Chemistry: A European Journal*, **18**, 13188-13194. <https://doi.org/10.1002/chem.201103221>
- [23] Langhals, H. and Fuchs, K. (2006) Fluorescent Labels for Aldehydes. *Collection of Czechoslovak Chemical Communications*, **71**, 625-634. <https://doi.org/10.1135/cccc20060625>
- [24] Langhals, H. and Wetzel, F. (2003) Perylene Pigments with Metallic Effects. Ger. Offen. DE 10357978 (Dec. 11, 2003).
- [25] Langhals, H. and Kirner, S. (2000) Novel Fluorescent Dyes by the Extension of the Core of Perylenetetracarboxylic Bisimides. *European Journal of Organic Chemistry*, 365-380. [https://doi.org/10.1002/\(SICI\)1099-0690\(200001\)2000:2<365::AID-EJOC365>3.0.CO;2-R](https://doi.org/10.1002/(SICI)1099-0690(200001)2000:2<365::AID-EJOC365>3.0.CO;2-R)
- [26] Tröster, H. (1983) Studies of the Protonation of Alkali Metal 3,4,9,10-Perylenetetracarboxylates. *Dyes and Pigments*, **4**, 171-177. [https://doi.org/10.1016/0143-7208\(83\)80015-1](https://doi.org/10.1016/0143-7208(83)80015-1)
- [27] Kaiser, H., Lindner, J. and Langhals, H. (1991) Synthesis of Nonsymmetrically Substituted Perylene Fluorescent Dyes. *Chemische Berichte*, **124**, 529-535. <https://doi.org/10.1002/cber.19911240319>
- [28] Chong, B., Moad, G., Rizzardo, E., Skidmore, M. and Thang, S.H. (2006) Thermolysis of RAFT-Synthesized Poly(Methyl Methacrylate). *Australian Journal of Chemistry*, **59**, 755-762. <https://doi.org/10.1071/CH06229>
- [29] Langhals, H. (1980) Dyes for Fluorescent Solar Collectors. *Nachrichten aus Chemie, Technik und Laboratorium*, **28**, 716-718. <https://doi.org/10.1002/nadc.19800281004>
- [30] Langhals, H., Schmid, T., Herman, M., Zwiener, M. and Hofer, A. (2012) Marking of Polymer Materials with Fluorescence Dyes for Their Clear Automatic Sorting. Ger. Offen. DE 102012012772.3 (June 22, 2012).
- [31] Włodarczyk, K.L., Ardron, M., Waddie, A.J., Taghizadeh, M.R., Weston, N.J. and Hand, D.P. (2017) Tamper-Proof Markings for the Identification and Traceability of High-Value Metal Goods. *Optics Express*, **25**, 15216-15230. <https://doi.org/10.1364/OE.25.015216>
- [32] Yashiki, K., Nagano, A., Sugihara, K. and Tashiro, T. (2017) Optical Element for Forgery-Proof. US Patent US20170334232.