Electronic Absorption Spectra and Third-Order Nonlinear Optical Property of Dinaphtho[2,3-b:2',3'-d]Thiophene-5,7,12,13-Tetraone (DNTTRA) and Its Phenyl diazenyl Derivatives: DFT Calculations

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How to cite this paper: Chen, Z.R., Zhang, Y.J., He, Z.R., Guan, Y.H., Li, Y. and Li, H.P. (2020) Electronic Absorption Spectra and Third-Order Nonlinear Optical Property of Dinaphtho[2,3-b:2',3'-d]Thiophene-5,7,12,13-Tetraone (DNTTRA) and Its Phenyl diazenyl Derivatives: DFT Calculations. *Computational Chemistry*, 8, 43-60.
<https://doi.org/10.4236/cc.2020.84005>

Received: October 10, 2020

Accepted: October 27, 2020

Published: October 30, 2020

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Abstract

Third-order nonlinear optical (NLO) materials have broad application prospects in high-density data storage, optical computer, modern laser technology, and other high-tech industries. The structures and frequencies of Dinaphtho[2,3-b:2',3'-d]thiophene-5,7,12,13-tetraone (DNTTRA) and its 36 derivatives containing azobenzene were calculated by using density functional theory B3LYP and M06-2X methods at 6-311++g(d, p) level, respectively. Besides, the atomic charges of natural bond orbitals (NBO) were analyzed. The frontier orbitals and electron absorption spectra of A-G5 molecule were calculated by TD-DFT (TD-B3LYP/6-311++g(d, p) and TD-M06-2X/6-311++g(d, p)). The NLO properties were calculated by effective finite field FF method and self-compiled program. The results show that 36 molecules of these six series are D- π -A- π -D structures. The third-order NLO coefficients γ (second-order hyperpolarizability) of the D series molecules are the largest among the six series, reaching 10^7 atomic units (10^{-33} esu) of order of magnitude, showing good third-order NLO properties. Last, the third-order NLO properties of the azobenzene ring can be improved by introducing strong electron donor groups (e.g. -N(CH₃)₂ or -NHCH₃) in the azobenzene ring, so that the third-order NLO materials with good performance can be obtained.

Keywords

Azobenzene, Dinaphtho[2,3-b:2',3'-d]Thiophene-5,7,12,13-Tetraone, Density

1. Introduction

Third-order nonlinear optical (NLO) materials have the characteristics of fast nonlinear optical response, large nonlinear polarizability, wide response band, high optical damage domain value, excellent flexibility, good chemical and thermal stability, and are easy to modify molecular structure. This kind of material has broad application prospects in high-density data storage, optical computer, modern laser technology, and other high-tech industries [1] [2] [3] [4]. Therefore, many chemists are attracted to design and synthesize new compounds with strong nonlinear optical effects. A large number of research results show that the third-order nonlinearity of materials is closely related to the type of molecular structure [5] [6]. For example, the linear and nonlinear polarizabilities of polyene and polymethine dyes have been shown to be highly correlated with the bond length alternation between adjacent C-C bonds in the conjugated chain. At present, the research focus of nonlinear optical materials is mainly focused on the construction of organic molecules containing electron donor (D), electron acceptor (A) and π -conjugation [7]. For example, D- π -A, A- π -D- π -A, D- π -A- π -D and other organic molecules [8] [9], focus on increasing the third-order NLO coefficients (second-order hyperpolarizability), so as to improve the optical properties of organic materials [10] [11] [12].

Quinone heterocyclic compounds are a kind of conjugated organic functional materials [13]. The intramolecular charge transfer compound synthesized by using it as the electron donor has become the preferred material for organic superconductors [14] [15] [16]. It is widely used in organic semiconductors, airport devices, organic light-emitting diodes, photovoltaic cells and other fields. At present, anthraquinone and naphthoquinone derivatives have been widely studied in the third-order nonlinear optical materials. The nonlinear optical effect of this kind of molecule mainly depends on its molecular configuration. The third-order hyperpolarizability of this kind of molecule increases obviously with the growth of its conjugated chain. At the same time, the sulfur-containing heterocycle in the conjugated heterocycle structure contributes significantly to its third-order hyperpolarizability due to its high hole mobility values and air stability, so it has attracted the attention of chemical researchers [17] [18] [19] [20] [21]. For example, Dibenzo [b,i] thiazene-5,7,12,14-tetraketone was synthesized from 2,3-dichloro-1,4-naphthoquinone and sodium sulfide by Gao's research group [13].

Azo aromatic organic compounds are a kind of nonlinear optical materials with good properties. Because of its photosensitivity and photoisomerism, it has a great potential application in nonlinear fields such as optical information sto-

rage [22]–[27]. Many researchers have studied its third-order nonlinear optical properties. For example, Guo *et al.* [28] study the third-order nonlinearity of materials by increasing π electron delocalization; Kang *et al.* [29] study the influence of different substituents on the nonlinear optical properties of azobenzene derivatives; Wang *et al.* [30] report that the introduction of other organic molecules on azobenzene molecules will enhance the nonlinear optical properties of azobenzene.

In recent years, there have been experimental and theoretical reports on the structure and NLO properties of quinone heterocycles containing diazobenzene [31] [32] [33] [34] [35]. DNTTRA has good rigid conjugate plane and good delocalization. The large π conjugated parent structure would interact with the azo group after conjugated bridging the electron donor of phenyl, which can further enhance the delocalization of the electron, and thus can be designed as an organic electron transport material. These structural molecules belong to D- π -A- π -D type organic molecules, and their chemical modification can improve the nonlinear optical properties of the molecules. Therefore, in this work, we calculated the molecular structure and third-order NLO of DNTTRA and 36 derivatives as shown in **Figure 1** and **Figure S1**. The effects of azobenzene on the third-order NLO properties of DNTTRA molecules at 3.9 sites, 2.9 sites, 2.10 sites, 1.8 sites, 1.11 sites and 4.8 sites were also discussed. Secondly, we further studied the introduction of -OH, -OCH₃, -NH₂, -NHCH₃, -N(CH₃)₂ into the para position of azobenzene ring. It provides a theoretical reference for the further design and synthesis of the third-order nonlinear optical materials containing DNTTRA with excellent properties.

2. Computational Details

The finite field (FF) method is an effective method for calculating the NLO properties of molecules [35] [36] [37]. In this paper, the structures of A-G5 molecule were optimized by using Gaussian 16 program at B3LYP/6-311++g(d, p) and M06-2X/6-311++g(d, p) computational level, which has been widely used in the NLO predictions [38] [39]. Based on the optimized structures, the electronic absorption spectra of these molecules were calculated by TD-M06-2X/6-311++g(d, p) method and the first superpolarizability (β_μ) in the dipole moment direction were calculated.

Then, the first hyperpolarizabilities (β_μ) of 37 molecules under different applied electric fields (0.001 - 0.004 a.u.) are calculated by using the finite field method and self-made program. Compared with the first hyperpolarizability (β_μ) in the direction of dipole moment when there is no applied electric field, the value of applied electric field corresponding to the closest value of the two is found. Then, under the external electric field, the components of the third-order nonlinear optical properties obtained by calculation are the credible values of the calculated molecules. Finally, the average values of the third-order NLO properties are calculated by using the following formulas (γ) [35]:

Figure 1. Chemical structure of DNTTRA and its 36 organic molecules.

$$\gamma = (\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2\gamma_{xxyy} + 2\gamma_{xxzz} + 2\gamma_{yyzz})/5 \quad (1)$$

where the γ_{xxxx} , γ_{yyyy} , γ_{zzzz} , γ_{xxyy} , γ_{xxzz} , γ_{yyzz} are the fourth-order tensor components. The center of thiophene ring is chosen as the coordinate origin when calculating the third-order NLO properties. The XY plane is a conjugate plane, the Z axis is perpendicular to the molecular plane, and the dipole moment of the molecule is roughly the same as the X axis.

3. Results and Discussion

3.1. Structures

The geometric optimization and frequency calculation of A-G5 molecule were carried out at the theoretical level of B3LYP/6-311++g (d, p) and M06-2X/6-311++g (d, p). Among the 37 molecules, A is C₂ point group and the rest are C₁ point group. Among the 37 molecules calculated, the length of C-C single bond ranges from 0.143 to 0.150 nm; whereas the single bond length of C-N ranges from 0.137 to 0.145 nm [9]. These structure parameters are similar with our previous works [37].

Among the 37 molecular structures, the dihedral angle of naphthalene and thiophene is between 2.5° and 4.8°, and the dihedral angle of naphthalene and azobenzene is between 1.4° and 1.8°, shown that the molecule is a quasi-planar molecule. Compared with B, C and D, the molecular planarity is poor. The degree of conjugation in conjugated system is consistent with the degree of overlap

of π -electron orbital, that is, the degree of overlap of π -electron orbital decreases when the degree of conjugation decreases, thus the charge transfer in molecule cannot be realized effectively, and the NLO effect of molecule is weakened. It can be predicted that the derivatives of azobenzene at 1.8 sites, 1.11 sites and 4.8 sites of DNTTRA molecule have less NLO properties than those of azobenzene at 2.9 sites, 3.9 sites, and 2.10 sites respectively.

3.2. Charge Analysis

In order to explore the correlation between charge transfer and NLO property of organic NLO materials, The charge of 11 organic molecules, such as B, C, D, E, F, G, D1, D2, D3, D4, D5, were calculated by natural bond orbital (NBO) method. The natural population analysis (NPA) charge values of each part of the molecule were listed in **Table 1**. Among them, I and III are benzene ring or phenyl derivative units, and II are conjugated bridges contained DNTTRA and two azo groups.

Table 1 shows that all the II structural units of 11 molecules are negatively charged. It is known that the conjugated bridge units of DNTTRA and two azo groups are electron acceptors. Compared with the parent D molecule, when R is -OH, -OCH₃, -NH₂, -NHCH₃, -N(CH₃)₂ and other groups, the negative charge of the II structure unit increases, but does not change its negative charge characteristics. I and III structural units are positively charged and play the role of electron donor in molecules, which will significantly influence the third-order NLO properties. Compared with the parent D molecule, when R is -OH, -OCH₃, -NH₂, -NHCH₃, -N(CH₃)₂ and other groups respectively, the positive charge increases, but does not change its positive charge characteristics. Therefore, these molecules can be regarded as D- π -A- π -D structures. With the enhancement of electron-donating ability of substituents introduced by para-position of benzene ring, the electron delocalization increases, which predicts that the third-order NLO properties of molecules will also be enhanced.

3.3. Frontier Orbitals and Electron Absorption Spectra

The molecular gap value is closely related to the intramolecular charge transfer [37]. In order to better understand the nature of molecular charge transfer, the B3LYP and M06-2X methods were used to calculate the energy gap of A-G5 molecules. The calculation results are shown in **Figure 2** and **Table S1**.

Table 1. NPA Charge distribution of 11 molecules.

Comp.	B	C	D	E	F	G	D1	D2	D3	D4	D5
Q(I)/e	0.216	0.216	0.215	0.212	0.213	0.218	0.241	0.245	0.263	0.274	0.280
Q(II)/e	-0.390	-0.390	-0.393	-0.418	-0.418	-0.375	-0.437	-0.447	-0.483	-0.507	-0.516
Q(III)/e	0.216	0.216	0.215	0.212	0.211	0.218	0.241	0.246	0.264	0.275	0.280

Figure 2. The molecular gap predicted by B3LYP and M06-2X in the current work.

It can be seen from **Figure 2** that the trend of energy gap calculated by the two methods is exactly the same. The energy gap of a molecule is the largest. B, C, D, E, F and G molecules all decrease in the order of A-G-E-F-B-C-D, that is to say, the D molecular energy gap obtained by introducing azobenzene into the 2.10 sites of A molecule is the minimum. Taking B, C, D, E, F and G as the parent molecules, introducing -OH, -OCH₃, -NH₂, -NHCH₃, -N(CH₃)₂ and other groups into the azobenzene para position respectively, the change trend of the energy gap values of the six series of derivative molecules is exactly the same, both of which decrease with the enhancement of electron donation ability. Among the six series, D series has the lowest energy gap. It is predicted that the series of molecules obtained by introducing azobenzene into the 2.10 sites of A molecule are most favorable for electronic transition.

Molecular orbitals play an important role in charge transfer. For the calcu-

lated six series B, C, D, E, F and G, the HOMO and LUMO electron orbital density distributions are similar. Therefore, **Figure 3** only shows the frontier orbital eigenvalues and frontier molecular orbital diagram of 12 molecules such as A, B, C, D, E, F, G and D1-D5. It can be seen from **Figure 3** that among the seven molecules A, B, C, D, E, F and G, although the increase of the eigenvalues of HOMO of D molecule is not the most, the decrease of the eigenvalues of LUMO is the largest, resulting in the minimum of the energy gap value. In the D1-D5 series, the eigenvalues of HOMO and LUMO orbitals increased in turn, but the eigenvalues of HOMO increased more, resulting in the decrease of energy gap value in turn. Based on this, it can be preliminarily predicted that with the enhancement of the molecular electron donation ability, the more obvious the intramolecular charge transfer will be. In addition to the F molecule, the HOMO electron orbital is mainly distributed on the azobenzene chain on both sides of DNTTRA. The lone pair electrons on the O and N atoms on the $-\text{OH}$, $-\text{OCH}_3$, $-\text{NH}_2$, $-\text{NHCH}_3$, $-\text{N}(\text{CH}_3)_2$ groups introduced by the azobenzene pair contribute to the HOMO electron orbital, all of which belong to the bonding π orbitals. The LUMO electron orbital of the molecule is mainly distributed on the DNTTRA

Figure 3. HOMO energies (E_H), LUMO energies (E_L) and HOMO-LUMO gaps (E_g) of A, B, C, D, E, F, G and D1-D5 derivatives.

conjugate surface, and they are π^* anti-bonding orbits. When electrons transit from HOMO to LUMO, the electron orbital concentrates from azobenzene side chain to DNTTRA. The results show that 18 molecules of B, C, D, E, F, G series have better intramolecular charge transfer effect.

The electronic absorption spectra of 12 molecules (A, B, C, D, E, F, G and D1-D5) are calculated by TD-M06-2X method, as shown in **Figure 4**, **Figure 5** and **Table S2**. It can be seen from **Figure 4** that among the seven molecules A, B, C, D, E, F and G, the wavelength of the lowest energy absorption peak of molecule A is 314 nm. B, C, D, E, F and G, are terminated with azobenzene at different positions on both sides of A molecule, and the conjugation range of the molecule increases, resulting in the red shift of the wavelength of the lowest energy absorption peak of the molecule. Especially, the wavelength of the

Figure 4. The electronic absorption spectra of A-G molecules.

absorption peak of D molecule substituted at 2.10 position is the largest (347 nm), which is nearly 100 nm compared with that of the parent A molecule. It is shown that the introduction of azobenzene at the 2.10 position of the parent a molecule is the most favorable for charge transfer, which is consistent with the conclusion of energy gap value analysis. **Figure 5** shows that with the D molecule as the parent, D1, D2, D3, D4 and D5 molecules obtained by introducing different electron donating groups into the para position of azobenzene ring, the wavelength of the lowest energy absorption peak increases in turn (significant red shift) with the enhancement of the electron donating ability of the substituent. This is mainly due to the difference in the nature of electronic transition. The absorption peaks of D1 originate from the HOMO-1 $\rightarrow$ LUMO + 1, HOMO-2 $\rightarrow$ LUMO + 2 and HOMO-4 $\rightarrow$ LUMO transitions of $S_0 \rightarrow S_7$; the

Figure 5. The electronic absorption spectra of D and D1-D5 molecules.

absorption peaks of D2 originate from the HOMO-1 $\rightarrow$ LUMO + 1, HOMO-3 $\rightarrow$ LUMO + 2 and HOMO-5 $\rightarrow$ LUMO transitions of $S_0 \rightarrow S_5$. The absorption peaks of D4 and D5 come from the mixed electronic transitions of $S_0 \rightarrow S_3$, HOMO-1 $\rightarrow$ LUMO + 1 and HOMO-4 $\rightarrow$ LUMO. To sum up, azobenzene was introduced into the two sides of DNTTRA, the introduction of azobenzene (D molecule) at the 2.10 sites is the most favorable for intramolecular charge transfer. After the azobenzene is terminated to the strong electron group (such as $-\text{NHCH}_3$ or $-\text{N}(\text{CH}_3)_2$), the electron transition energy is relatively reduced, the lowest energy absorption peak is significantly red shifted, and the electron is easy to be excited. Therefore, it can be predicted that the azobenzene has strong third-order NLO properties.

3.4. Third-Order NLO Properties

Using the finite field FF method, an electric field ranging from 0.001 to 0.004 a.u. which applies in both of the negative and positive X, Y, Z directions (the change range is set to 0.00025 to 0.0005 a.u.), it is explored that the first hyperpolarizability (β_μ) of each molecule under applied electric field is closest to the corresponding value of applied electric field. In addition, the non-zero components and average values of the third-order polarizability of 37 molecules calculated under electric field are shown in **Table 2**.

Table 2 shows that the γ_{xxxx} of the third-order polarizability of 37 molecules is the largest, indicating that the third-order NLO properties of DNTTRA derivatives are mainly due to charge transfer in the X-axis direction. Compared with molecule A, the third-order NLO coefficients (γ) increased significantly when azobenzene was introduced at 3.9 sites, 2.9 sites, 2.10 sites, 1.8 sites, 1.11 sites, and 4.8 sites respectively. The third-order NLO coefficient (γ) of azobenzene is the largest when azobenzene is introduced at 2.10 sites. The third-order NLO coefficients (γ) of azobenzene at 3.9 sites, 2.9 sites and 2.10 sites are much larger than those of azobenzene at 1.8 sites, 1.11 sites and 4.8 sites. The results show that azobenzene at 1.8 sites, 1.11 sites and 4.8 sites is not as good as azobenzene at 3.9 sites, 2.9 sites and 2.10 sites, which is consistent with the structural coplanarity analysis of the preceding molecules. The best substitution of azobenzene for A molecule is at 2.10 sites. Among the six series of substituted derivatives such as B, C, D, E, F and G, the third-order NLO coefficient (γ) of the three series derivatives such as B, C and D is obviously larger than that of the three series derivatives such as E, F and G. The third-order NLO coefficients of D series derivatives are the largest in the six series of substituted derivatives, reaching 10^7 order of magnitude atomic units (10^{-33} esu), showing good third order NLO properties. The third-order NLO coefficients (γ) of each series of derivatives have the same change rule, that is, they increase in turn according to the substitution of OH, $-\text{OCH}_3$, $-\text{NH}_2$, $-\text{NHCH}_3$, $-\text{N}(\text{CH}_3)_2$. This is mainly due to the induction effect and conjugation effect of the introduced donor electrons. $-\text{N}(\text{CH}_3)_2$ and $-\text{NHCH}_3$ have strong electron-donating induction and conjugation effects, while $-\text{OH}$ and $-\text{OCH}_3$ have relatively weak induction and conjugation effects.

Table 2. The third-order NLO properties of 37 molecules (in 10^5 a.u.).

Comp.	γ_{xxxx}	γ_{xxyy}	γ_{xxzz}	γ_{yyyy}	γ_{yyzz}	γ_{zzzz}	γ
A	3.39	0.30	0.17	0.26	0.05	0.14	0.97
B	26.31	2.89	0.27	0.40	0.13	0.27	7.11
C	29.13	3.31	0.12	1.31	0.13	0.19	7.55
D	21.59	7.33	0.27	3.99	0.40	0.67	8.45
E	9.63	2.22	0.49	2.72	0.25	0.74	3.80
F	11.87	3.13	1.25	2.50	0.63	1.25	5.13
G	5.68	0.99	0.25	3.46	0.25	0.37	2.49
B1	51.87	1.25	2.50	0.63	1.25	3.75	13.25
B2	58.75	1.25	1.25	3.13	1.88	1.88	14.50
B3	72.50	0.63	-1.87	0.00	-1.25	-3.75	12.75
B4	120.63	1.25	0.00	1.53	0.00	-6.25	24.75
B5	96.79	3.95	3.95	3.95	3.95	7.90	26.47
C1	43.29	6.25	0.63	0.50	1.88	6.25	13.37
C2	52.49	6.25	0.00	2.50	0.00	-1.25	13.25
C3	65.10	6.88	-0.63	0.63	-0.63	-0.63	15.25
C4	85.01	8.75	-0.63	0.63	-1.25	-1.25	19.63
C5	106.25	100.01	-2.50	1.25	-1.25	-2.50	23.50
D1	29.85	12.79	3.20	11.73	3.52	3.20	16.76
D2	32.50	12.50	1.25	6.88	2.51	3.75	15.13
D3	35.56	15.80	-1.97	13.83	0.00	1.98	15.81
D4	57.34	24.58	0.00	20.48	0.00	0.00	25.40
D5	95.80	30.62	0.12	17.07	0.12	0.37	34.40
E1	10.00	3.75	0.00	6.88	1.25	1.25	5.63
E2	16.25	5.01	1.25	5.01	0.00	0.00	6.75
E3	11.85	3.96	0.00	1.98	0.00	-1.98	3.95
E4	18.13	6.41	-1.07	5.33	-3.19	-2.13	5.12
E5	21.73	11.85	0.00	13.83	1.98	1.98	13.04
F1	12.79	2.13	0.00	4.26	1.06	-1.06	4.48
F2	14.99	4.37	0.62	5.62	1.25	1.25	6.88
F3	16.89	2.82	-1.02	3.58	-0.77	-1.28	4.25
F4	20.26	2.13	-1.06	4.26	-1.07	-1.07	4.69
F5	30.00	5.62	1.25	4.99	0.00	1.25	10.01
G1	6.87	0.00	1.25	1.25	-0.63	0.63	2.01
G2	8.97	1.95	1.17	3.90	1.17	1.17	4.53
G3	8.12	1.25	0.00	3.12	0.63	1.25	3.25
G4	11.25	0.63	-0.63	1.87	-1.25	-1.25	1.63
G5	13.75	2.50	-1.25	5.00	0.63	-1.25	4.25

Therefore, the third-order NLO coefficient (γ) of $\text{N}(\text{CH}_3)_2$ and $-\text{NHCH}_3$ mainly depends on the electron-donating ability of azobenzene para-substituents. Azobenzene was introduced at the 2.10 sites of DNTTRA, and strong donor electron groups $-\text{N}(\text{CH}_3)_2$ and $-\text{NHCH}_3$ were introduced at azobenzene para-position. These molecules can be designed as third-order NLO materials with good properties.

4. Conclusion

The structures and frequencies of 37 azobenzene derivatives such as DNTTRA (A molecule) and B-G5 were calculated by M06-2X methods at 6-311++g(d, p) computational level. The natural bond orbital (NBO) method was used to calculate the charge distribution of 11 organic molecules such as B, C, D, E, F, G, D1, D2, D3, D4 and D5. The results show that the 36 molecules of six series are D- π -A- π -D structure. The planarity of the three series of molecules obtained by introducing azobenzene at 2.10 sites, 3.9 sites, and 2.9 sites of A molecule is better than that of substituted at 1.8 sites, 1.11 sites, and 4.8 sites. The γ value of the third-order NLO coefficient of the molecule also increases obviously, reaching 10^7 order of magnitude atomic units (10^{-33} esu), showing good third-order NLO properties. Compared with 3.9 sites, 2.9 sites, 1.8 sites, 1.11 sites, and 4.8 sites substituted azobenzene (D) terminated at the 2.10 sites of A molecule, the minimum energy absorption peak wavelength of B, C, E, F and G molecule increased significantly. The γ value of the third-order NLO coefficient of the molecule increased by 1.1 - 3.4 times, indicating that the introduction of azobenzene at 2.10 sites of molecule A is better than that at 3.9 sites, 2.9 sites, 1.8 sites, 1.11 sites, and 4.8 sites. The third-order NLO properties of the azobenzene ring can be improved by terminating the strong donor electron groups (e.g. $-\text{NHCH}_3$ or $-\text{N}(\text{CH}_3)_2$) in the azobenzene ring, so that the third-order NLO materials with good properties can be obtained.

Acknowledgements

This work is financially supported by the Project of Science and Technology Department of Sichuan Province (No. 2015GZ0343); the Project of Sichuan Provincial Department of Education (Nos. 15ZA0346, 17ZA0346); the National Natural Science Foundation of China (No. 21808092), A Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions. This research work is supported by the high performance computing platform of Jiangsu University.

Conflicts of Interest

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

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Supporting Information

Figure S1. The optimized structures of A-G molecules.

Table S1. Eigenvalues of frontier orbitals for 37 molecules (in eV·mol⁻¹).

Comp.		E1	E2	E3	E4	E5	F1	F2	F3	F4	F5
B3LYP	E _(HOMO)	-6.474	-6.355	-5.964	-5.731	-5.620	-6.410	-6.277	-5.881	-5.644	-5.533
	E _(LUMO)	-3.512	-3.457	-3.345	-3.274	-3.246	-3.539	-3.486	-3.381	-3.312	-3.285
	E _g	2.962	2.898	2.619	2.457	2.374	2.871	2.791	2.500	2.332	2.248
M06-2X	E _(HOMO)	-7.725	-7.599	-7.163	-6.906	-6.744	-7.644	-7.519	-7.080	-6.819	-6.661
	E _(LUMO)	-2.607	-2.563	-2.479	-2.423	-2.390	-2.634	-2.591	-2.513	-2.458	-2.426
	E _g	5.118	5.036	4.684	4.483	4.354	5.010	4.928	4.567	4.361	4.235
Comp.		G1	G2	G3	G4	G5					
B3LYP	E _(HOMO)	-6.504	-6.376	-6.001	-5.798	-5.678					
	E _(LUMO)	-3.623	-3.576	-3.464	-3.397	-3.371					
	E _g	2.881	2.800	2.537	2.401	2.307					
M06-2X	E _(HOMO)	-7.754	-7.619	-7.208	-6.941	-6.797					
	E _(LUMO)	-2.710	-2.671	-2.592	-2.556	-2.529					
	E _g	5.044	4.948	4.616	4.385	4.268					

Table S2. The data of electronic absorption spectrum for E, F and G.

Comp.	Electronic transition	λ /nm	E/ev	f	Major contribution
E	$S_0 \rightarrow S_1$	488.4	2.54	0.0011	HOMO-3 $\rightarrow$ LUMO + 2 (34%)
					HOMO-2 $\rightarrow$ LUMO + 3 (29%)
					HOMO-2 $\rightarrow$ LUMO (10%)
	$S_0 \rightarrow S_7$	325.5	3.81	0.5763	HOMO-1 $\rightarrow$ LUMO (39%)
					HOMO $\rightarrow$ LUMO + 1 (16%)
					HOMO-2 $\rightarrow$ LUMO (12%)
F	$S_0 \rightarrow S_1$	488.2	2.54	0.0006	HOMO-3 $\rightarrow$ LUMO + 2 (46%)
					HOMO-3 $\rightarrow$ LUMO + 3 (17%)
					HOMO-3 $\rightarrow$ LUMO (11%)
	$S_0 \rightarrow S_7$	324.2	3.82	0.4107	HOMO-1 $\rightarrow$ LUMO (42%)
					HOMO-1 $\rightarrow$ LUMO + 1 (12%)
					HOMO-3 $\rightarrow$ LUMO (13%)
G	$S_0 \rightarrow S_1$	486.8	2.55	0.0001	HOMO-3 $\rightarrow$ LUMO + 2 (38%)
					HOMO-2 $\rightarrow$ LUMO + 3 (32%)
					HOMO-2 $\rightarrow$ LUMO + 1 (7%)
	$S_0 \rightarrow S_{15}$	286.6	4.33	0.4945	HOMO-7 $\rightarrow$ LUMO (25%)
					HOMO $\rightarrow$ LUMO + 2 (18%)
					HOMO-1 $\rightarrow$ LUMO + 3 (16%)
					HOMO $\rightarrow$ LUMO (13%)