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Synthesis and characterization of naphthalene diimide (NDI)-based near infrared chromophores with two-photon absorbing properties

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ABSTRACT

A new series of 2,7-bis-(2-ethylhexyl)-benzo[*lmn*][3,8]-phenanthroline-1,3,6,8-tetraone (NDI) based pseudo-quadrupolar molecules (**1**–**6**) is presented and their two-photon absorption (2PA) cross-sections measured with the Z-scan method. The spectral properties of these compounds can be fine-tuned via modification of the donor segments. The corresponding 2PA cross-section (σ_2) values at the most readily available 800 nm excitation range from 229±15 to 1092±59 GM owing to differences in conjugation length and/or position of substitution.

1. Introduction

Two-photon absorbing chromophores are of current research interest due to their potential applications in photodynamic therapy,[1] scanning excitation microscopy,[2] and three-dimensional optical data storage,[3] etc. In addition, bio-imaging techniques based on two-photon absorption methods are superior to those based on single-photon absorption[4] owing to better in-depth penetration, minimum cell damage, and higher spatial resolution.[5] In recent years, a wide array of donor–acceptor–donor (D–A–D) and donor–π-donor (D–π-D) compounds[6] have been synthesized to attain high two-photon absorption cross-section (σ_2). The results of structure property relationship studies reveal that σ_2 values increase with increasing donor/acceptor strength, conjugation length, and better planarity of the π center.[7] In yet another approach, to expand the utility of two-photon absorbing materials in areas, such as biomarkers and biomedical applications, it is favorable to develop chromophores with emission wavelength in the red or near-IR region (e.g., 700–1200 nm); otherwise, the auto-fluorescence of the cells would be interfering, especially in the blue-green range. Previously, we reported dibutoxydi-benzo[*a*,*c*]phenazine derivatives exhibiting promising σ_2 values.[8] In continuation of our efforts[9] on the preparation of chromophores with high σ_2 values, we report herein the synthesis and characterization of naphthalene diimide (NDI) based D–A–D type molecules. In particular, they are strategically designed to be near-IR emitting and capable of absorbing two-photons.

NDI has attracted much interest because of its thermal stability, good electron accepting properties, and solution processability.[10] Moreover, the electronic properties can be fine-tuned by introducing substituents at either the naphthalene core or the

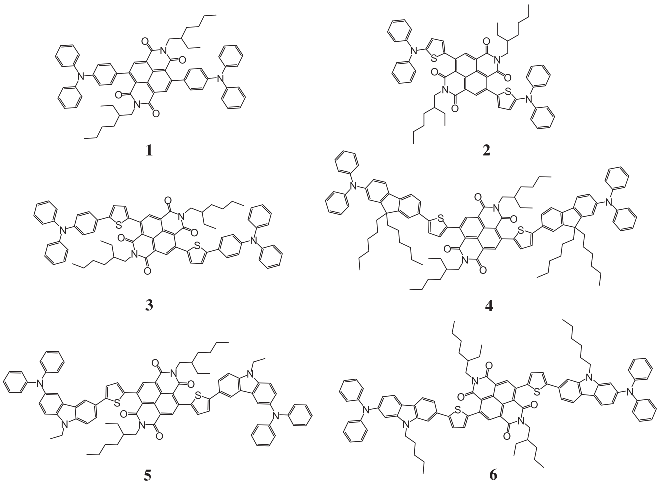

Fig. 1. Structures of compounds **1**–**6**.

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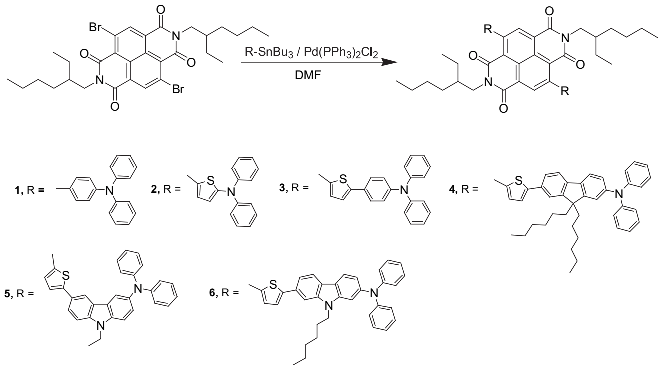
nitrogen atom of the imide group.[11] The NDI containing materials have been extensively used as organic field effect transistors,[12] supramolecular assemblies,[13] molecular switches,[14] and sensors.[15] In this work, we have successfully synthesized a series of two-photon absorbing chromophores **1**–**6** (Fig. 1) that consist of triarylamines and an NDI-based core of 2,7-bis-(2-ethylhexyl)-benzo[*lmn*][3,8]-phenanthroline-1,3,6,8-tetraone acting as the electron donors and acceptor, respectively.

2. Results and discussions

2.1. Synthetic procedures

The synthetic routes of the titled compounds are depicted in Scheme 1. In brief, bromination of 1,4,5,8-naphthalene tetracarboxylic dianhydride using dibromocyanuric acid in concentrated sulfuric acid led to the formation of the intermediate 2,6-dibromonaphthalene 1,4,5,8-tetracarboxylic dianhydride. 4,9-Dibromo-2,7-bis(2-ethylhexyl)benzo[*lmn*]-[3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-tetraone was then prepared by reacting 2-ethyl-hexyl amine in the presence of acetic acid.[16] Further Stille's cross-coupling reaction of the obtained dibromo compound with appropriate stannyl reagents afforded the desired products in good yield (>65%).



Scheme 1. Synthesis of compounds **1**–**6**.

2.2. One-photon spectra and electrochemical studies

Absorption and emission spectra of compounds **1**–**6** are depicted in Fig. 2 and Fig. S1 (see Supplementary data), respectively, and pertinent data are summarized in Table 1. All the compounds exhibit two major prominent absorption bands appearing at 380–387 nm and 592–617 nm. The former one is ascribed to a localized aromatic π–π* transition and the latter is of charge-transfer (CT) character.[8,16,17] The peak wavelength of the lowest energy absorption attributable to the charge-transfer transition increases in the order of **1**<**3**<**2**, in consistent with the trend observed for 11,12-dibutoxydibenzo[*a*,*c*]phenazine bridged amines.[8] The combination of diphenyl amino entity and thiophene ring constitutes a stronger electron donor such that the HOMO of **2** is pushed to the highest energy and accordingly the absorption onset is greatly red-shifted to >825 nm. In comparison, non-coplanarity between the phenylene ring plus thiophene and the NDI core results in less effective interaction between the donor and the acceptor. Further replacing the phenyl ring in **3** with fluorene or carbazole moieties, forming **4**–**6**, the charge-transfer absorption profiles at >500 nm remain approximately the same, indicating that the effective conjugation length is not increased by simply extending the conjugation network. The trend of the corresponding fluorescence spectra is consistent with that observed in the absorption spectra. Note that the emission quantum yields are relatively low owing to the operation of energy gap law.[18] Generally, smaller S_0–S_1 energy gap leads to better overlap of the vibrational wavefunctions between S_1 and S_0 states and hence accelerated internal conversion (IC), which leads to fast nonradiative deactivation.

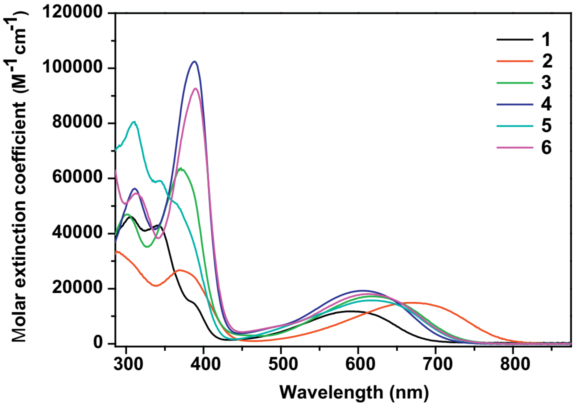


Fig. 2. Absorption spectra of compounds **1**–**6** in toluene at room temperature.

Table 1
Photophysical and redox properties for compounds **1**–**6**

	λ_{abs} (10^{-4} ϵ)[a] [nm]	λ_{em}[a] [nm]	Φ_f [a,b] [%]	E_{ox}[c] [V]	E_{red}[c] [V]	HOMO/ LUMO (E_{gap}) [eV]	σ_2[d] [GM]
1	590 (1.18) 400 (0.90) 340 (4.30) 306 (4.61)	741	0.23	+0.57	−1.17 −1.53	5.36/ 3.60 (1.76)	229 ±15
2	673 (1.49) 400 (1.90) 368 (2.67)	N/A	—	+0.38 +0.48	−1.12 −1.51	5.17/ 3.66 (1.51)	—
3	620 (1.72) 400 (3.27) 371 (6.37) 302 (4.69)	776	0.02	+0.45 +1.05	−1.07 −1.49	5.25/ 3.62 (1.63)	982 ±41
4	606 (1.93) 400 (8.40) 388 (10.24) 310 (5.63)	780	0.08	+0.37 +0.90	−1.09 −1.53	5.17/ 3.49 (1.67)	624 ±27
5	616 (1.58) 400 (2.23) 343 (5.92) 310 (8.06)	787	0.03	+0.23 +0.80	−1.09 −1.50	5.03/ 3.37 (1.66)	1092 ±59
6	614 (1.81) 400 (7.91) 390 (9.26) 312 (5.46)	766	0.03	+0.34 +0.83	−1.05 −1.48	5.14/ 3.43 (1.70)	651 ±32

[a] Measured in toluene. ϵ: molar extinction coefficients.
[b] λ_{ex}=500 nm. DCM (4-(dicyanomethylene)-2-methyl-6-(*p*-dimethylaminostyryl)-4*H*-pyran, λ_{em}=615 nm) in MeOH, with Φ of 0.43, served as the reference.
[c] Measured in CH_2Cl_2. Potentials are quoted with reference to the internal reference, ferrocene ($E_{1/2}$=+256 mV vs Ag/AgNO$_3$).
[d] Averaged value of five replicas measured with the Z-scan method at 800 nm.

The electrochemical properties of compounds **1**–**6** are also compiled in Table 1 while cyclic voltammograms and differential pulse voltammograms of **1** and **4** are shown in Fig. 3. The two reversible reduction waves observed correspond to the sequential injection of electrons into the imides.[19] Except for **1**, all other compounds exhibit two oxidation potentials originating from the end-capping thiophene ring and the arylamine. The presence of single oxidation wave in **1** likely stems from the absence of the thiophene ring. The peak separation between the first and second oxidation waves in **2** is much smaller than that in **3**–**5**, implying that electrons are less delocalized in **2** compared to others. The first oxidation potential is used to calculate the highest occupied molecular orbital (HOMO) energy level of the molecules (cf.

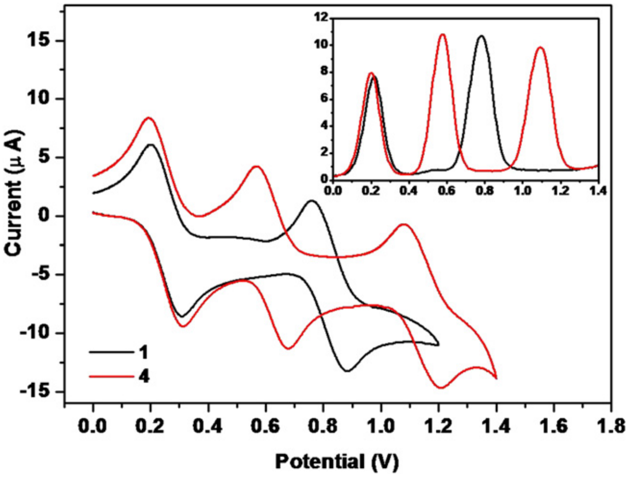


Fig. 3. Cyclic voltammograms of **1** and **4** in CH_2Cl_2. Reference electrode: nonaqueous $Ag/AgNO_3$; supporting electrolyte: 0.1 M tetrabutylammonium hexafluorophosphate; scan rate: 100 mV s^{-1}. The peaks of the lowest potential are due to internal ferrocene. Inset: Differential pulse voltammograms of **1** and **4**.

ferrocene 4.8 eV).[20] These HOMO values along with the absorption onset are then used to obtain the lowest unoccupied molecular orbital (LUMO) energy levels[21] listed in Table 1.

2.3. Two-photon absorption

Two-photon absorption cross-sections (σ_2) of **1** and **3**–**6** in toluene were determined by the open-aperture Z-scan method[22] using the most readily available 800 nm Ti/Sapphire femtosecond laser excitation. Compound **2** was not investigated because of its overlapping one-photon absorption at 800 nm. Fig. 4 shows the experimental results for compounds **1** and **5**, and all the cross-section values are tabulated in Table 1. The σ_2 values are in the order of **1**<**4**–**6**<**3**<**5**. Typically, the σ_2 value increases with conjugation length and depends on the nature of the aryl spacer between the donor and acceptor segments. Extended π-conjugation may result in a greater density of population for both electronic and vibrational states, providing more effective coupling channels between ground and two-photon allowed states,[23] the result of which would in turn increase the 2PA cross-section. For **1** and **3**, it can be seen that extending the π-conjugation simply by adding one thiophene ring significantly enhances the σ_2 value from 229 to 982 GM (10^{-50} cm^4 s $photon^{-1}$). As for the comparison among **3**–**6**, for which the effect of elongated conjugation is not significant, the results may be rationalized by the theoretical expression of σ_2 in Eq.1,[1a]

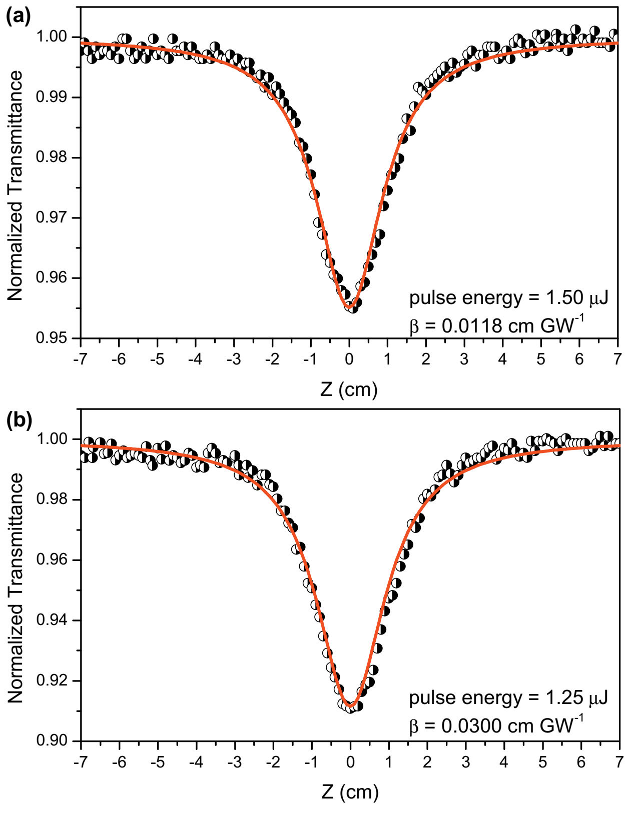


Fig. 4. Z-scan experimental data of compounds (a) **1** (2.15×10^{-3} M) and (b) **5** (1.21×10^{-3} M) in toluene with 800 nm excitation.

$$\sigma_{2(\max)} = \frac{2\pi h\nu^2 L^4}{\epsilon_0^2 n^2 c^2}\left(\frac{1}{\Gamma}\right)S_{fg}$$

with

$$S_{fg} = \left[\sum_{i}\frac{\left\langle \mu_{gi}\mu_{if}\right\rangle}{(E_{gi}-h\nu)}\right]^2 = \frac{1}{5}\left[\left(\frac{\Delta\mu_{gf}\mu_{gf}}{h\nu}\right)^2 + \sum_{i\neq f,g}\left(\frac{\mu_{gi}^2\mu_{if}^2}{(E_{gi}-h\nu)^2}\right)\right] \tag{1}$$

where subscripts g, f and i denote the ground, final, and an assisting intermediate state, respectively; μ stands for the amplitude of the transition dipole moment between the specified states; $\Delta\mu_{gf}$ is the change in the static dipole moment in the final state relative to the ground state; *n* represents the refractive index and $L=(n^2+2)/3$.

In these pseudo-quadrupolar molecules, $\Delta\mu_{gf}$ is minimized and the second term becomes dominant. In this study with 800 nm excitation, the lowest lying charge-transfer transition centered around 600 nm serves as an intermediate state *i* to assist with 2PA. For **3** and **4**, the one-photon extinction coefficients (see Fig. 2 and Table 1) of the charge-transfer band remain much of the same, implying similar μ_{gi} values. On the other hand, the absorption profiles <450 nm are distinct, with **3**<**4** in the extinction coefficient, suggesting that the varying σ_2 values may be resulting from different μ_{if}. It is worthy to note that higher electronically excited states are often congested, among which states with vanishing one-photon oscillator strengths may be responsible for 2PA and act as the final state *f* in quadrupolar molecules or nearly symmetric pseudo-quadrupolar ones.[24] For instance, it is calculated (Table S1, Chart S1, and Figures S2) that for compound **3** at wavelengths below 408 nm, some states with oscillator strength <0.01 emerge (Table S2). As for compounds **4**–**6**, owing to their larger molecular frameworks, those states are found beyond S_{10} and are not reported. Compound **6** (651 GM) has a similar σ_2 value to **4**, plausibly because the carbazolyl nitrogen does not contribute π-electron density to the spacer due to its *meta*-disposition. On the other hand, **5** has a slightly higher σ_2 value (1092 GM). Unlike **6**, compound **5** possesses a diphenyl amino entity trans to the carbazolyl nitrogen, which significantly increases the electron-donating strength of the carbazole–amine composite. This viewpoint is further supported by the lowest oxidation potential for **5** among all. Clearly, both the site of substitution and variation of the aryl spacer affect the efficiency of charge redistribution from the donor to the acceptor. In addition, for compounds **3**–**6** with comparable charge-transfer character, a general trend is observed that higher σ_2 value at 800 nm (**5**>**3**>**6**>**4**) is correlated to smaller one-photon absorption extinction coefficient at 400 nm (**4**>**6**>**3**>**5**). In other words, the two-photon allowed and one-photon forbidden states, which contribute less to the UV–vis absorption spectrum, are pinpointed.

The σ_2 values at 800 nm in these compounds are relatively small compared to 2PA chromophores with 11,12-dibutoxydibenzo[*a*,*c*]-

phenazine as the electron acceptor core.[8] Nevertheless, their near-IR emission provides better penetration. Conversely, these compounds have larger σ_2 values than congeners with a 2,1,3-benzothiazole core,[6a] suggesting the importance of a stronger acceptor in enhancing the 2PA effect.

3. Conclusion

In conclusion, we have synthesized a new series of D–A–D type compounds with NDI-based acceptor core and *N*,*N*-aryl amino group terminal donors. Their photophysical properties can be fine-tuned by playing on the nature, either length or position of substitution, of the conjugated spacers between donor and central acceptor moieties. All these compounds show moderate to strong 2PA cross-sections (229–1092 GM) that are comparable to other reported D–A–D type analogues. More importantly, the corresponding emissions are all in the near-IR region (>740 nm). We thus believe that the present system will serve as a building block for developing materials suitable for two-photon imaging.

4. Experimental section

4.1. General procedures

Unless otherwise specified, all the reactions were performed under nitrogen atmosphere using standard Schlenk techniques. All solvents used were purified by standard procedures, or purged with nitrogen before use. ^{1}H NMR spectra were recorded on a Bruker 400 MHz spectrometer operating at 400.135 MHz. Absorption and emission spectra were recorded on a Cary 50 probe UV–vis spectrophotometer and an Edinburgh (FS920) fluorimeter, respectively. All chromatographic separations were carried out on silica gel (60 M, 230–400 mesh). Mass spectra (FAB) were recorded on a VG70-250S mass spectrometer. Cyclic voltammetry experiments were performed with a CH Instruments electrochemical analyzer. All measurements were carried out at room temperature with a conventional three electrode configuration consisting of a platinum working electrode, a platinum wire auxiliary electrode, and a nonaqueous Ag/AgNO$_3$ reference electrode. The $E_{1/2}$ values were determined as $(E_{pa}+E_{pc})/2$, where E_{pa} and E_{pc} are the anodic and cathodic peak potentials, respectively. The potentials are quoted against the ferrocene internal standard. The solvent in all experiments was CH$_2$Cl$_2$, and the supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate. Elementary analyses were performed on a Perkin–Elmer 2400 CHN analyzer.

4.2. Synthetic details and characterization

4,9-Dibromo-2,7-bis(2-ethylhexyl)benzo-[*lmn*][3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-tetraone, *N*,*N*-di-phenyl-4-(tributyl-stannyl) aniline, *N*,*N*-diphenyl-5-(tributyl-stannyl)thio-phen-2-amine, *N*,*N*-diphenyl-4-(5-(tributyl-stannyl)thiophen-2-yl)aniline, 9-ethyl-*N*,*N*-diphenyl-7-(5-(tributylstannyl)thio-phen-2-yl)-9*H*-carbazol-2-amine, 9,9-dihexyl-*N*,*N*-diphenyl-7-(5-(tributylstannyl)thiophen-2-yl)-9*H*-fluoren-2-amine, 9-hexyl-*N*,*N*-diphenyl-7-(5-(tributylstannyl)-thiophen-2-yl)-9*H*-carbazol-2-amine were prepared by adopting reported procedures.[8,25] The final compounds **1**–**6** were obtained with similar processes, for which an illustrative example is given below for **1**. Characterizations of compounds **2**–**6** are also included.

*4.2.1. 4,9-Bis(4-(diphenylamino)phenyl)-2,7-bis(2-ethylhexyl)benzo[lmn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone (**1**).* 4,9-Dibromo-2,7-bis(2-ethylhexyl)benzo[*lmn*]-[3,8]phenan-throline-1,3,6,8(2*H*,7*H*)-tetraone (0.64 g, 1.0 mmol), *N*,*N*-diphenyl-4-(tributylstannyl)aniline (1.17 g, 2.2 mmol), and Pd(PPh$_3$)$_2$Cl$_2$ (20 mg) were charged in a 100 mL round-bottom flask. Under a nitrogen atmosphere, a 10 mL of DMF was added and the contents were heated to 80 °C and maintained at this temperature for 12 h. After the reaction was complete the reaction mixture was diluted with methanol. The precipitate obtained was filtered, washed with methanol, and dried. The residue was then purified by column chromatography on silica gel using CH$_2$Cl$_2$/hexanes (1:3) mixture as the eluent to give **1** as a blue solid in 70% yield. FABMS (*m*/*z*): 976.4 [M]$^+$; ^{1}H NMR (CDCl$_3$) δ: 0.81–0.89 (m, 12H), 1.24–1.36 (m, 16H), 1.85–1.88 (m, 2H), 4.0–4.10 (m, 4H), 7.05–7.13 (m, 8H), 7.19–7.21 (m, 8H), 7.26–7.31 (m, 12H), 8.65 (s, 2H). ^{13}C NMR (CDCl$_3$) δ: 10.9, 14.4, 23.4, 24.3, 28.9, 31.0, 38.1, 44.6, 122.3, 122.7, 123.9, 125.5, 125.7, 127.6, 129.7, 130.0, 133.8, 136.5, 147.5, 147.7, 148.4, 163.2, 163.4. Anal. Calcd for $C_{66}H_{64}N_4O_4$: C, 81.12; H, 6.60; N, 5.73. Found: C, 81.03; H, 6.57; N, 5.88.

*4.2.2. 4,9-Bis(5-(diphenylamino)thiophen-2-yl)-2,7-bis(2-ethylhexyl) benzo[lmn][3,8] phenanthroline-1,3,6,8(2H,7H)-tetraone (**2**).* Yield: 68%. FABMS (*m*/*z*): 988.41 [M]$^+$; ^{1}H NMR (CDCl$_3$) δ: 0.80–0.87 (m, 12H), 1.22–1.34 (m, 16H), 1.82–1.88 (m, 2H), 4.0–4.10 (m, 4H), 6.59–6.60 (d, 2H, J=4.0 Hz), 7.07–7.10 (m, 4H), 7.23–7.24(m, 2H), 7.27–7.32 (m, 16H), 8.71 (s, 2H). ^{13}C NMR (CDCl$_3$) δ: 10.6, 14.1, 23.0, 24.0, 28.7, 30.8, 37.8, 44.5, 117.7, 121.1, 123.8, 124.2, 124.9, 127.3, 132.0, 136.2, 139.4, 147.3, 156.3, 162.9. Anal. Calcd for $C_{62}H_{60}N_4O_4S_2$: C, 75.27; H, 6.11; N, 5.66. Found: C, 75.17; H, 6.07; N, 5.86.

*4.2.3. 4,9-Bis(5-(4-(diphenylamino)phenyl)thiophen-2-yl)-2,7-bis(2-ethylhexyl)benzo[lmn][3,8] phenanthroline-1,3,6,8(2H,7H)-tetraone (**3**).* Yield: 75%. FABMS (*m*/*z*): 1140.47 [M]$^+$; ^{1}H NMR (CDCl$_3$) δ: 0.80–0.87 (m, 12H), 1.22–1.34 (m, 16H), 1.82–1.88 (m, 2H), 4.0–4.10 (m, 4H), 7.02–7.06 (m, 7H), 7.11–7.13 (m, 8H), 7.24–7.29 (m, 11H), 7.32–7.33 (d, 2H, J=3.6 Hz), 7.49–7.51 (d, 4H, J=8.8 Hz), 8.79 (s, 2H). ^{13}C NMR (CDCl$_3$) δ: 11.1, 14.5, 23.5, 24.4, 29.0, 31.1, 38.2, 45.0, 122.8, 123.0, 123.7, 123.7, 125.2, 125.7, 127.2, 127.9, 128.1, 129.8, 130.7, 137.0, 139.5, 140.1, 147.8, 148.2, 148.3, 163.0, 163.1. Anal. Calcd for $C_{74}H_{68}N_4O_4S_2$: C, 77.86; H, 6.00; N, 4.91. Found: C, 77.87; H, 6.00; N, 5.01.

*4.2.4. 4,9-Bis(5-(7-(diphenylamino)-9,9-dihexyl-9H-fluoren-2-yl) thiophen-2-yl)-2,7-bis(2-ethylhexyl)benzo[lmn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone (**4**).* Yield: 70%. MALDI MS (*m*/*z*): 1655.38 [M+H]$^+$; ^{1}H NMR (CDCl$_3$) δ: 0.62–0.94 (m, 32H), 1.06–1.16 (m, 24H), 1.24–1.40 (m, 16H), 1.82–1.96 (m, 10H), 4.07–4.16 (m, 4H), 6.09–7.02 (m, 6H), 7.11–7.13 (m, 10H), 7.22–7.26 (m, 10H), 7.37–7.38 (d, 2H, J=3.6 Hz), 7.43–7.44 (d, 2H, J=3.6 Hz), 7.55–7.62 (m, 8H), 8.84 (s, 2H). ^{13}C NMR (CDCl$_3$) δ: 10.9, 14.3, 14.3, 22.8, 23.3, 24.0, 24.2, 28.9, 29.9, 30.9, 31.8, 38.0, 40.6, 44.9, 55.4, 119.4, 119.8, 120.3, 120.7, 122.8, 123.4, 123.8, 124.1, 125.2, 125.6, 127.8, 130.5, 132.2, 135.9, 136.8, 139.6, 140., 141.5, 147.7, 148.2, 149.0, 151.7, 152.7, 162.9. Anal. Calcd for $C_{112}H_{124}N_4O_4S_2$: C, 81.31; H, 7.55; N, 3.39. Found: C, 81.30; H, 7.56; N, 3.50.

*4.2.5. 4,9-Bis(5-(6-(diphenylamino)-9-ethyl-9H-carbazol-3-yl)thiophen-2-yl)-2,7-bis(2-ethylhexyl) benzo[lmn][3,8]phenanthroline-1,3,6,8 (2H,7H)-tetraone (**5**).* Yield: 80%. FABMS (*m*/*z*): 1374.57 [M]$^+$; ^{1}H NMR (CDCl$_3$) δ: 0.85–0.92 (m, 12H), 1.25–1.39 (m, 16H), 1.45–1.49 (m, 6H), 1.91–1.94 (m, 2H), 4.05–4.12 (m, 4H), 4.35–4.37 (m, 4H), 6.94 (t, 4H, J=6.7 Hz), 7.09–7.11 (m, 8H), 7.20–7.24 (m, 7H), 7.29–7.40 (m, 11H), 7.74–7.77 (m, 2H), 7.92 (s, 2H), 8.21–8.22 (m, 2H), 8.82 (s, 2H). ^{13}C NMR (CDCl$_3$) δ: 11.1, 14.4, 14.5, 23.5, 24.4, 29.0, 31.1, 38.2, 45.0, 109.4, 110.0, 118.7, 119.3, 122.1, 122.6, 122.8, 123.2, 123.6, 124.2, 124.8, 125.5, 125.7, 126.3, 127.9, 129.5, 130.9, 137.0, 138.0, 139.2, 140.1, 140.7, 149.1, 149.8, 163.1. Anal. Calcd for $C_{90}H_{82}N_6O_4S_2$: C, 78.57; H, 6.01; N, 6.11. Found: C, 78.05; H, 6.08; N, 5.98.

4.2.6. 4,9-Bis(5-(7-(diphenylamino)-9-hexyl-9H-carbazol-2-yl)thiophen-2-yl)-2,7-bis(2-ethylhexyl)benzo[lmn][3,8]phenanthroline-

*1,3,6,8(2H,7H)-tetraone (**6**).* Yield: 65%. FABMS (*m*/*z*): 1487.71 $[M]^+$; ^{1}H NMR ($CDCl_3$) δ: 0.86–0.94 (m, 18H), 1.19–1.40 (m, 28H), 1.76–2.02 (m, 6H), 4.10–4.17 (m, 8H), 6.95–6.99 (m, 6H), 7.02–7.15 (m, 10H), 7.23–7.27 (m, 8H), 7.40–7.41 (d, 2H, *J*=3.6 Hz), 7.46–7.53 (m, 4H), 7.58 (s, 2H), 7.9–7.99 (m, 4H), 8.85 (s, 2H). ^{13}C NMR ($CDCl_3$) δ: 10.9, 14.2, 14.3, 22.7, 23.3, 24.2, 27.1, 28.9, 29.1, 30.9, 31.8, 38.0, 43.2, 44.9, 105.1, 106.1, 117.5, 117.9, 118.6, 120.3, 121.2, 122.6, 122.8, 123.3, 123.5, 124.2, 125.6, 127.8, 129.4, 130.6, 130.9, 136.8, 139.7, 139.9, 141.4, 142.5, 146.8, 148.4, 149.5, 162.9. Anal. Calcd for $C_{98}H_{98}N_6O_4S_2$: C, 79.10; H, 6.64; N, 5.65. Found: C, 79.00; H, 6.69; N, 6.00.

4.3. Open-aperture Z-scan

The open-aperture Z-scan experiments were conducted with the experimental setup and fitting procedures described in literature.[22] In this study, a mode-locked Ti/Sapphire laser (Tsunami, Spectra Physics) produced single Gaussian pulses, which were then coupled to a regenerative amplifier that generated ~180 fs, 1 mJ pulses (800 nm, 1 kHz, Spitfire Pro, Spectra Physics). The pulse energy, after proper attenuation, was reduced to 0.75–1.50 μJ and the repetition rate was further reduced to 20 Hz. After passing through an *f*=30 cm lens, the laser beam was focused and passed through a 1.00 mm cell filled with the sample solution (1.01×10^{-3}–2.15×10^{-3} M) and the beam radius at the focal position was 5.09×10^{-3} cm. When the sample cell was translated along the beam direction (*z*-axis), the transmitted laser intensity was detected by a photodiode (PD-10, Ophir).

4.4. Quantum chemistry computation

The structures of the molecules were optimized using B3LYP/6-31G*. For each molecule, a number of possible conformations were examined and the one with the lowest energy (i.e., global minimum) was used. For the excited state, we employed the time-dependent density functional theory (TDDFT) with the B3LYP functional. All of them were performed with Q-Chem 3.0 software.[26] There exist a number of previous works that employed TDDFT to characterize excited states with charge-transfer character.[27] In some cases underestimation of the excitation energies was seen.[27,28] Therefore, in the present work, we use TDDFT to characterize the extent of the charge-shift and avoid drawing conclusions from the excitation energy.

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Supplementary data

Contained within are the emission spectra, details of the fitting procedures for the z-scan method and quantum chemistry computation, as well as the ^{1}H and ^{13}C NMR spectra. Supplementary data associated with this article can be found in online version, at doi:10.1016/j.tet.2010.09.041. These data include MOL files and InChIKeys of the most important compounds described in this article.

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