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Energy-level modulation of organic alkynes by click chemistry

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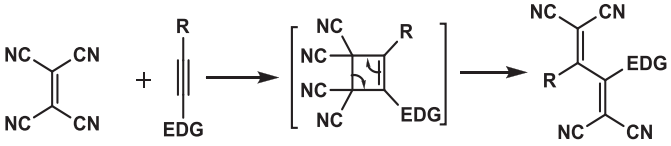
ABSTRACT

A series of novel donor–acceptor chromophores have been successfully synthesized in excellent yield by metal-free [2+2] click chemistry, which was effective in the energy-level modulation. Structures of the conjugated compounds were fully characterized by NMR, IR, and MS. By introducing TCNE, TCNQ, F_4-TCNQ click monomers, we obtained energy-level tunable materials in high solubility, which was beneficial for processing. It has been demonstrated that the absorption characteristics of all the newly prepared compounds have been strongly bathochromically shifted with an end-absorption far into the near infrared region due to the efficient intramolecular charge-transfer (CT) interaction. The electrochemical properties have been studied by cyclic voltammograms indicating good agreement between the electrochemical and optical band gaps determined by the end absorption.

1. Introduction

Energy-level modulation of organic photoelectric materials has received tremendous research attention in both academic interests and commercial applications, such as solar cells and organic lighting emitting display (OLED).[1] Tuning of the electronic HOMO and LUMO levels is crucial in improving the optoelectronic properties of organic materials. However, the use of organic photoelectric materials with controllable charge transport is still in its infancy, and it remains a major challenge to effectively tune the charge transport. Fortunately, design of new donor–acceptor type π-conjugated molecules is one solution,[2] which can be achieved by the thermal [2+2] cycloaddition followed by the ring-opening of click chemistry.

Click chemistry provides efficient, reliable, and selective reactions for synthesizing new compounds and to generate combinatorial libraries.[3] Nowadays the most popular and well-studied click reaction is the copper (I)-catalyzed azide–alkyne cycloaddition reaction (CuAAC), forming a triazole ring[4] by Sharpless[5] and Meldal,[6] which has been widely used for the preparation of functional materials.[7] However, the development of other click-type reactions has simultaneously been pursued,[8] typically thermal [2+2] cycloadditions, followed by retro-electrocyclization, of tetracyanoethene (TCNE),[9] 7,7,8,8-tetracyanoquiodimethane (TCNQ),[10] and 2,3,5,6-tetrafluoro-7,7,8,8-tetra cyanoquinodimethane (F_4-TCNQ) to 'electronically confused' alkynes. For example, when dialkylanilino groups are employed as the electron-donating group (EDG), a [2+2] cycloaddition followed by the ring opening reaction proceeds in the quantitative yield under mild conditions (Scheme 1).[11]



Scheme 1. Click chemistry-type addition reaction between TCNE and alkynes activated by electron-donating group (EDG).

The [2+2] click reactions are with significant advantages that the products feature strong charge-transfer (CT) interactions in the visible absorption region, potent redox activities,[12] and are useful for optimization of the electronic states, thereby leading to the enhanced performance of the optoelectronic devices, such as photovoltaic cells.[13]

In the present work, we designed and synthesized a family of organic conjugated molecules with great potential applications for photoelectric materials. Meanwhile, the novel click chemistry allowed us to efficiently modulate the HOMO–LUMO energy band gap, leading to π-conjugated molecules with tunable electrochemical properties as well as excellent solubility, which was beneficial for processing.

2. Results and discussion

2.1. Synthesis

The reacting aromalkyne molecules **C1**–**C4** were shown in Scheme 2. **C1**, **C3**, and **C4** were synthesized according to the

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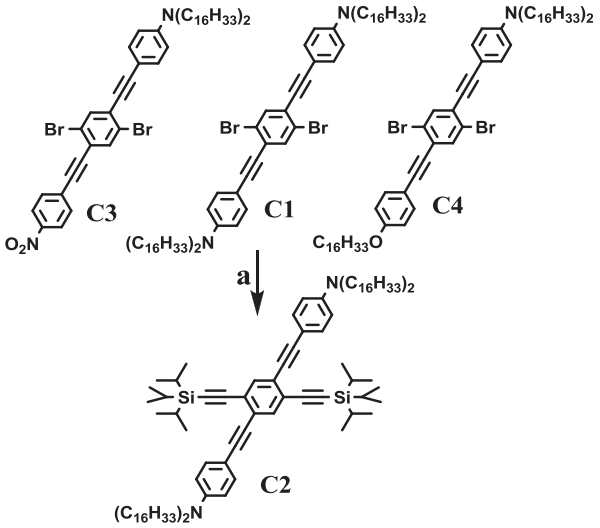


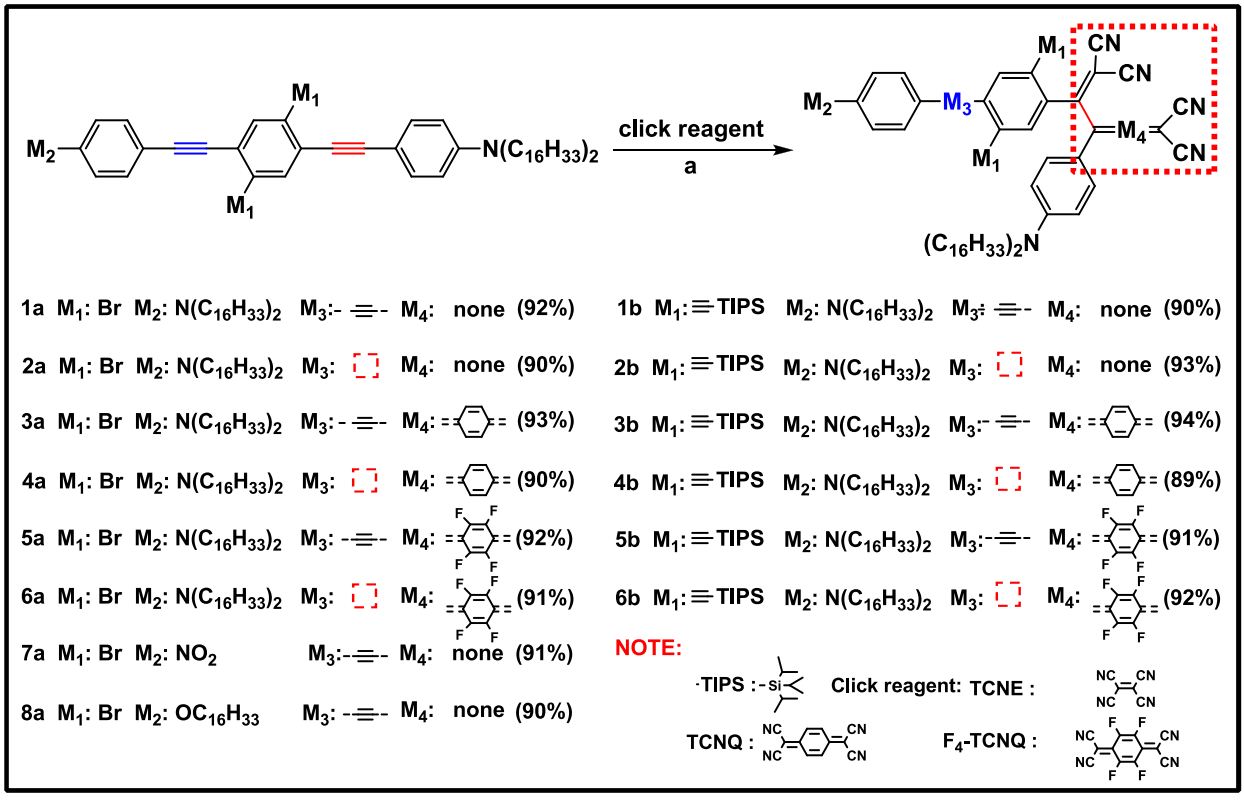
Scheme 2. Structures of **C1**–**C4** and their synthesis routes: (a) ethynyltriisopropylsilane, $Pd(PPh_3)_4$, CuI, THF, diisopropylamine (i-Pr_2NH), 80 °C, 12 h.

literature methods,[14] while **C2** monomer was newly synthesized and fully characterized by NMR, IR, and MS spectra from which the chemical structures were verified. Compounds **C1**–**C4** have good solubility in common organic solvents.

Synthesis of donor–acceptor chromophores **1a**–**8a** and **1b**–**6b** was achieved through introducing in amine-substituted aromatic precursors by the high-yielding [2+2] click reactions using TCNE, TCNQ, and F_4-TCNQ as acceptor molecules. As it was shown in Scheme 3, the click reaction was selective, namely, all the acetylenic bonds with red high light reacted with the electron acceptor, such as TCNE, while the blue ones were alternative. The click reactions required heating in dichlorobenzene up to 100 °C for 1 h with significantly high yields ranging from 89% to 94%. In fact, the reactions with click reagent TCNE could be fulfilled under ambient temperature and enhancement of temperature to 100 °C was just for higher efficiency. All the newly prepared products were in high purity, which was confirmed by NMR, IR, and MS spectra. Moreover, they were stable at ambient temperature under air and reasonably soluble in common organic solvents, such as CH_2Cl_2, acetone, and acetonitrile, which was beneficial for processing. Furthermore, no special purification process was necessary because of the absence of byproducts. Therefore, this kind of reaction satisfied most of the requirements of click chemistry, and it could be classified as a new metal-free click chemistry that further improved optoelectronic properties of organic materials.

2.2. UV–vis spectroscopy

The normalized UV–vis absorption spectra were shown in Fig. 1. The spectral shapes and positions were very similar to the reported click products.[15] Most of the prepared products showed intense CT bands with end-absorptions reaching into the near infrared region. Aromoalkyne **C1** reacting with different click reagents TCNE, TCNQ, and F_4-TCNQ yielded **1a**, **3a**, and **5a**, respectively (Fig. 1(a)). The electron-withdrawing groups tended to bathochromically shift the spectra relative to **C1**, and the shift in the end absorption (λ_{end}) from that of **C1** (417 nm) was 128, 371, and 551 nm for **1a**, **3a**, and **5a**, respectively. Comparing **3a** with **1a**, the intensification of conjugation was much larger, and the intramolecular charge transferred over a longer conjugation length along the molecular backbones, so the CT bands were red shifted. Although the conjugation length of **3a** and **5a** was similar, the introduction of the strong electron-withdrawing group F into **5a** further lowered the LUMO energy



Scheme 3. Synthesis of donor–acceptor chromophores: (a) dichlorobenzene, 100 °C, 1 h.

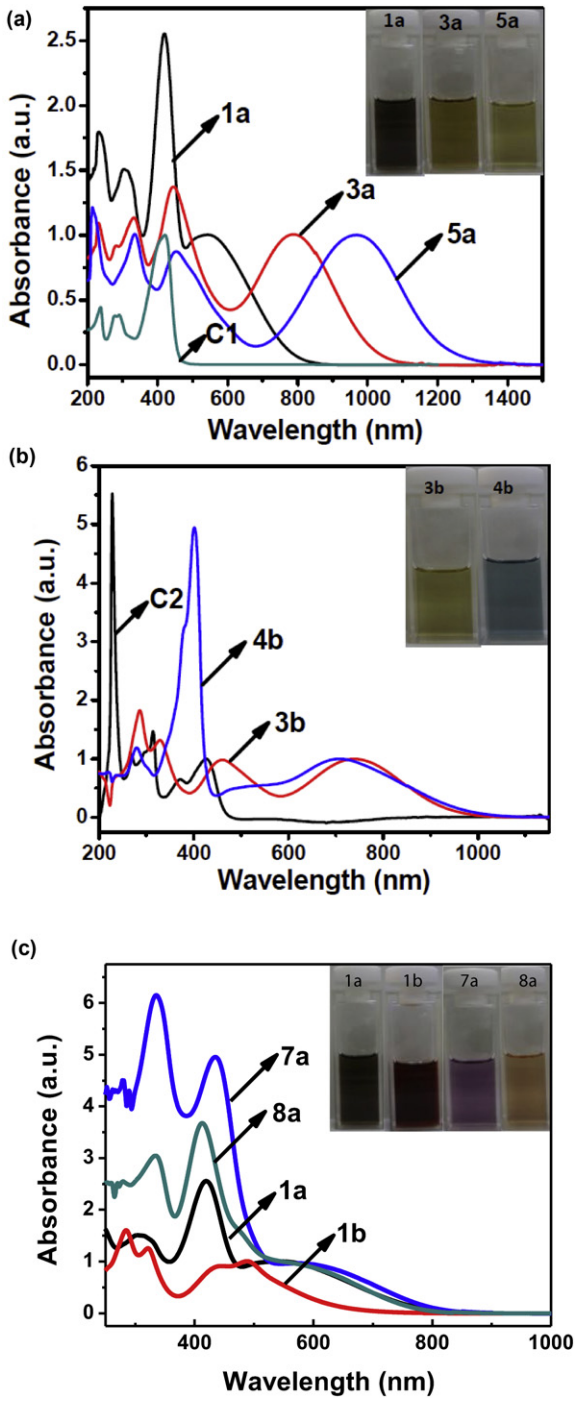


Fig. 1. UV–vis absorption spectra of (a) **C1**, **1a**, **3a**, and **5a**; (b) **C2**, **3b**, and **4b**; (c) **1a**, **1b**, **7a**, and **8a** in CH_2Cl_2 at 298 K. The inset photographs showed the colors of the corresponding solutions.

level and band gap, and enhanced the electron affinity, so the redshift was more significant. Thus, the extent of the shift increased in the sequence of **1a**<**3a**<**5a**.

The positions of λ_{end} also depended on the number of click reagents (Fig. 1(b)). Compounds **3b** and **4b** were synthesized by introduction of one or two TCNQ in monomer **C2**, respectively. In comparison with **C2** (425 nm), **3b** (736 nm) and **4b** (709 nm) both lowered the energy of the CT bands, which was due to the introduction of the electron-withdrawing group CN, while the extent of bathochromical shifts was similar. Compound **3b** exhibited only 27 nm more of redshifts than **4b** which was the co-impact of the conjugation length and the number of electron-withdrawing group CN. Namely, although **4b** had two more CN groups than **3b**, which benefited the diminution of the band gap, the triple bond reacting with the second TCNQ decreased the conjugation length so that the band gap decrease was inhibited.

Fig. 1(c) exhibited the absorption spectra of products of different monomers **C1**–**C4** reacting with the same click reagent (TCNE). The extent of bathochromical shift depended not only on the conjugation length of the main chains but also the electron-withdrawing ability of the substituents. As the electron-withdrawing ability increased in the order of TIPS<$OC_{16}H_{33}$<Br<NO_2, correspondingly, the redshift increased in the sequence of **1b**<**8a**<**1a**<**7a**. Thus, electron-rich substituents shifted the CT bands bathochromically.

According to Fig. 2, the resulting donor–acceptor chromophores featured well-defined CT bands in the visible region. Subsequently, the reaction of **C3** was initially investigated by UV–vis spectroscopic titration experiments by adding acceptor molecule TCNE to **C3** in chlorinated solvents. When TCNE was selected as a compact acceptor molecule, the reaction immediately proceeded at 100 °C, suggesting the occurrence of click functionalization. Thus, the absorption intensities of the precursor (**C3**) started to decrease and a new CT band with a relatively weak peak at 599 nm shown due to the occurrence of click product **7a**. The peak position of the CT bands was unchanged, while the intensities linearly increased with the increasing amount of the added TCNE. The presence of the isosbestic points at 354 and 493 nm for **C3** indicated no side reactions. Similarly, the same titration experiments were carried out for **C4**. Very interestingly, when the intense CT absorption was noted, the peak top values shifted bathochromically with increasing amount of TCNE addition. The possibility of the intermolecular aggregation was ruled out.

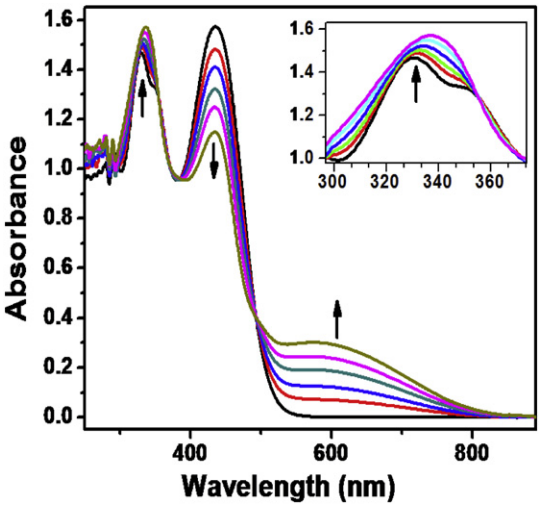


Fig. 2. UV–vis spectral changes of **C3** upon titration with TCNE (0–1.0 equiv) in chloroform at 20 °C. Inset: zoom on the low energy CT band.

If the side-chain chromophores did not interact with each other, the peak top values should be constant.[16] This result suggested that this click-type reaction could affect the electronic state of the whole conjugated compounds[14] thus could be employed for tuning the energy levels of the conjugated materials.

2.3. Electrochemistry

One of the most important features of donor–acceptor chromophores was the oxidation/reduction activities. To clarify the electrochemical properties, the electrochemical behavior of

products and reactants was examined by cyclic voltammetry (CV). Cyclic voltammogram of **7a** was shown in Fig. 4, and all the others were set in the Supplementary data. The energy levels were calculated using the Ferrocene (Fc) value of −4.8 eV with respect to the vacuum level, which was defined as zero. The measured oxidation potential of Fc (vs Ag/AgCl) was 0.46 V. Therefore, the E_{HOMO} levels of the products could be calculated by the equation $E_{HOMO}=-e[U_{onset(ox)}-U_{1/2,Fc}+4.8\ V]$ and the LUMO energy (E_{LUMO}) levels could be estimated by the equation $E_{LUMO}=-e[U_{onset(red)}-U_{1/2,Fc}+4.8\ V]$, where $U_{1/2,Fc}$ standards for the half-wave potential of Fc/Fc^{+}.

compounds exhibited smaller electrochemical band gaps E_g^b than TCNE-products, which was probably caused by the expanded π-conjugation of the acceptor moieties and strongly electron-withdrawing ability.

3. Conclusions

A series of stable derivatives were prepared by the [2+2] cycloaddition of TCNE, TCNQ, and F_4-TCNQ to donor-substituted alkynes in excellent yields, and fully characterized. The results

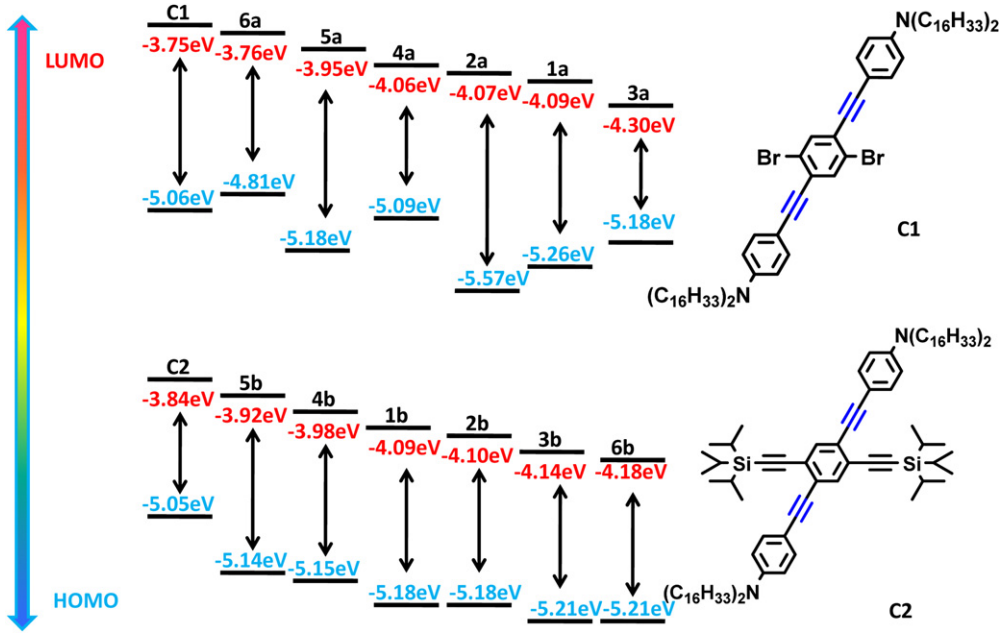


Fig. 3. HOMO and LUMO energy levels of **C1**, **C2** and products **1**–**6a**, **1**–**6b**. On the right are the chemical structures of **C1** and **C2**.

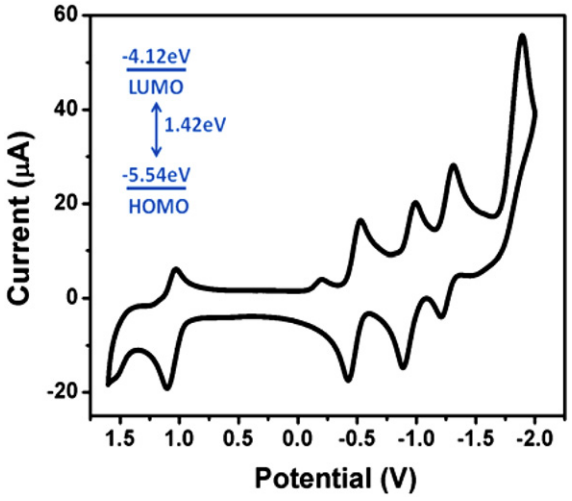


Fig. 4. Cyclic voltammogram of **7a** in CH_2Cl_2/Bu_4NPF_6 at 20 °C. Inset: HOMO and LUMO of product **7a**.

For all the materials, multi-reversible oxidation potentials and reduction potentials were observed in CH_2Cl_2. Onset oxidation/reduction potentials, band gaps, LUMO and HOMO levels were listed in Table 1 and Fig. 3, respectively. Compared with the reactants, the resulting compounds showed anodically shifted first reduction potentials (E_{on}^{red}). The anodic shift of $E_{red,1}$ could be explained by the efficient interaction of aromatic precursors with the acceptors, which made the reduction more easy. TCNQ and F_4-TCNQ

obtained by UV–vis spectra of these pure compounds indicated the efficient intramolecular charge-transfer (CT) interactions, which was in result of the enlargement of the absorption spectrum and the corresponding CT bands strongly bathochromically shifted with an end-absorption reaching far into the near infrared region. Meanwhile, the energy level of the products was effectively modulated by the novel metal-free [2+2] click reaction which further improved optoelectronic properties of organic materials. Moreover, all the newly prepared compounds were in high solubility, which contributed greatly to the processability. Therefore, the brand-new products synthesized in this paper have great potential for the application as optoelectronic materials, and will be worthwhile for future projects.

4. Experimental section

4.1. General

Reagents were purchased from commercial sources (Aldrich) and used without further purification. Monomers **C1**, **C3**, and **C4** were synthesized according to the literature methods.[13] ^1H NMR and ^{13}C NMR spectra were measured on a Bruker AV300 NMR spectrometer (300 MHz) at 20 °C. Chemical shifts are reported in parts per million downfield from $SiMe_4$, using the solvent's residual signal as an internal reference. FT-IR was recorded on a Perkin–Elmer LR-64912C Fourier transform infrared spectrometer. All MALDI-TOF-MS spectra were measured on a Shimadzu AXIMA-CFR mass spectrometer. The operation was performed at an accelerating

Table 1
Electrochemical properties of the products **1**–**8a**, **1**–**6b** and reactants **C1**–**C4**

Materials	E_{on}^{ox} [a] (eV)	E_{on}^{red} [a] (eV)	E_g [b] (eV)	Energy level (eV)		E_g [c] (eV)	Materials	E_{on}^{ox} [a] (eV)	E_{on}^{red} [a] (eV)	E_g [b] (eV)	Energy level (eV)		E_g [c] (eV)
				HOMO	LUMO						HOMO	LUMO	
1a	0.69	−0.48	1.17	−5.26	−4.09	1.51	**1b**	0.61	−0.48	1.09	−5.18	−4.09	1.72
2a	1.00	−0.50	1.50	−5.57	−4.07	1.47	**2b**	0.61	−0.47	1.08	−5.18	−4.10	2.08
3a	0.61	−0.27	0.88	−5.18	−4.30	1.17	**3b**	0.64	−0.43	1.07	−5.21	−4.14	1.24
4a	0.52	−0.51	1.03	−5.09	−4.06	1.17	**4b**	0.58	−0.59	1.17	−5.15	−3.98	1.24
5a	0.61	−0.62	1.23	−5.18	−3.95	1.02	**5b**	0.57	−0.65	1.22	−5.14	−3.92	1.11
6a	0.24	−0.81	1.05	−4.81	−3.76	0.96	**6b**	0.64	−0.39	1.03	−5.21	−4.18	1.01
7a	0.97	−0.45	1.42	−5.54	−4.12	1.53	**8a**	0.97	−0.48	1.45	−5.54	−4.09	1.50
C1	0.49	−0.82	1.31	−5.06	−3.75	2.73	**C2**	0.48	−0.73	1.21	−5.05	−3.84	2.62
C3	0.55	−1.11	1.66	−5.12	−3.46	2.32	**C4**	0.49	−0.99	1.48	−5.06	−3.58	2.77

[a] Onset potentials determined from cyclic voltammograms in CH_2Cl_2/Bu_4NPF_6 at a scan rate of 40 mV/s.
[b] Band gap calculated from the energy level of cyclic voltammograms.
[c] Band gap estimated from the onset wavelength of optical absorption in CH_2Cl_2 solution.

potential of 20 kV by a linear positive ion mode with dithranol as a matrix. UV–vis spectra were recorded in a quartz cuvette on a JASCO V-570 spectrophotometer. Cyclic voltammetric measurements were carried out in a conventional three-electrode cell using Glassy Carbon working electrodes of 2 mm diameter, a platinum wire counter electrode, and an Ag/AgCl reference electrode on a computer-controlled CHI 660C instrument at rt.

*4.1.1. 4,4′-((2,5-Bis((triisopropylsilyl)ethynyl)-1,4-phenylene)bis(ethyne-2,1-diyl))bis(N,N-dihexadecylaniline) (**C2**).* The monomer **C1** (1.36 g, 1.00 mmol) cross-coupled with (triisopropylsilyl)acetylene (0.54 g, 3.00 mmol) was dissolved in *i*-Pr_2NH/THF 1:1 (40 mL). After the solution was purged with bubbling Ar for 30 min, $Pd(PPh_3)_4$ (70 mg, 0.06 mmol) and CuI (23 mg, 0.12 mmol) were added. The reaction mixture was then stirred at rt for 12 h under Ar. The mixture was concentrated, rediluted with CH_2Cl_2, and filtered through a plug of silica gel. The solvent was removed in vacuo and the crude product was purified by column chromatography (SiO_2, hexane/CH_2Cl_2 10:1) to give **C2** (1.03 g, 66%) as a yellow solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ=0.89 (m, 12H), 1.16 (m, 42H), 1.28 (s, 104H), 1.56 (m, 8H), 3.28 (m, 8H), 6.55 (d, *J*=8.4 Hz, 4H), 7.36 (d, *J*=8.4 Hz, 4H), 7.59 (s, 2H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ=11.4, 14.1, 18.8, 22.7, 27.1, 27.2, 29.3, 29.5, 29.6, 29.7, 31.9, 50.9, 85.7, 96.2, 96.6, 105.0, 108.5, 111.0, 124.5, 125.2, 133.1, 136.0, 148.1 ppm. FT-IR (KBr): ν=2924, 2853, 2193, 1605, 1521, 1466, 1367, 1193, 1136, 882, 810 cm^{-1}. MALDI-TOF-MS (dithranol): *m*/*z*: calcd for $C_{108}H_{184}N_2Si_2$: 1565.4 g mol^{-1}, found: 1566.5 g mol^{-1} $[MH]^+$; elemental analysis calcd (%) for $C_{108}H_{184}N_2Si_2$ (1565.4): C 82.79, H 11.84, N 1.79, Si 3.59; found: C 82.80, H 11.86, N 1.78.

*4.1.2. 2-(2,5-Dibromo-4-((4-(dihexadecylamino)phenyl)ethynyl)phenyl)-3-(4-(dihexadecylamino)phenyl)buta-1,3-diene-1,1,4,4-tetracarbonitrile (**1a**).* The monomer **C1** (0.136 g, 0.100 mmol) and click reagent TCNE (0.128 g, 1.00 mmol) were dissolved in dichlorobenzene (1 mL). The reaction mixture was then stirred at 100 °C for 1 h under Ar. The mixture was concentrated, rediluted with CH_2Cl_2, and filtered through a plug of silica gel. The solvent was removed in vacuo and the crude product was purified by column chromatography (SiO_2, CH_2Cl_2) to give **1a** (0.0822 g, 92%) (the productivity was calculated by removing the amount of the monomer that unreacted or reacted with two click reagents) as a brown solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ=0.88 (m, 12H), 1.26 (s, 104H), 1.58 (m, 8H), 3.29 (m, 4H), 3.36 (m, 4H), 6.57 (d, *J*=8.7 Hz, 2H), 6.64 (d, *J*=8.7 Hz, 2H), 7.39 (d, *J*=8.4 Hz, 2H), 7.63 (s, 1H), 7.65 (d, *J*=9.3 Hz, 2H), 7.79 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): δ=14.1, 22.7, 26.9, 27.0, 27.1, 27.2, 29.3, 29.4, 29.5, 29.6, 31.9, 51.0, 51.4, 85.6, 94.5, 103.4, 106.5, 110.7, 111.1, 111.5, 111.9, 113.7, 114.7, 118.5, 121.3, 121.3, 124.1, 132.1, 132.6, 133.3, 133.7, 134.7, 137.4, 149.0, 152.9, 162.1, 165.9 ppm; FT-IR (KBr): ν=2923, 2852, 2211, 2190, 1604, 1568, 1522, 1484, 1466, 1415, 1402, 1368, 1293, 1207, 1183, 1144, 1060, 816, 720 cm^{-1}. MALDI-TOF-MS (dithranol): *m*/*z*: calcd for $C_{92}H_{142}Br_2N_6$: 1488.97 g mol^{-1}, found: 1489.8 g mol^{-1} $[MH]^+$; elemental analysis calcd (%) for $C_{92}H_{142}Br_2N_6$ (1488.97): C 74.06, H 9.59, N 5.63; found: C 74.08, H 9.56, N 5.64.

*4.1.3. 2-(4-(Dihexadecylamino)phenyl)-3-(4-((4-(dihexadecylamino)phenyl)ethynyl)-2,5-bis((triisopropylsilyl)ethynyl)phenyl)buta-1,3-diene-1,1,4,4-tetracarbonitrile (**1b**).* The molar amount of the reactants, the reaction condition and the yield calculation method were all the same as **1a**. The crude product was purified by column chromatography (SiO_2, CH_2Cl_2) to give **1b** (0.0763 g, 90%) as a dark red solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ=0.88 (m, 12H), 1.20 (m, 42H), 1.26 (s, 104H), 1.56 (m, 8H), 3.35 (m, 8H), 6.62 (d, *J*=9.3 Hz, 4H), 7.58 (s, 2H), 7.83 (d, *J*=9.2 Hz, 4H) ppm. FT-IR (KBr): ν=2925, 2855, 2216, 2191, 1604, 1579, 1523, 1483, 1466, 1417, 1367, 1243, 1211, 1183, 1103, 997, 883, 813, 720 cm^{-1}. MALDI-TOF-MS (dithranol): *m*/*z*: calcd for $C_{114}H_{184}N_6Si_2$: 1693.41 g mol^{-1}, found: 1694.3 g mol^{-1} $[MH]^+$; elemental analysis calcd (%) for $C_{114}H_{184}N_6Si_2$ (1693.41): C 80.79, H 10.94, N 4.96; found: C 80.80, H 10.98, N 4.97.

*4.1.4. 2-(2,5-Dibromo-4-(1,1,4,4-tetracyano-3-(4-(dihexadecyl amino)phenyl)buta-1,3-dien-2-yl)phenyl)-3-(4-(dihexadecyl amino) phenyl)buta-1,3-diene-1,1,4,4-tetracarbonitrile (**2a**).* Except that the click reagent molar amount was twice as that of the monomer, all the other conditions were the same as **1a**. The crude product was purified by column chromatography (SiO_2, CH_2Cl_2/ethyl acetate=20:1) to give **2a** (0.146 g, 90%) as a light brown solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ=0.88 (m, 12H), 1.26 (s, 104H), 1.58 (m, 8H), 3.37 (m, 8H), 6.66 (d, *J*=9.3 Hz, 4H), 7.64 (d, *J*=9.0 Hz, 4H), 7.77 (s, 2H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): δ=14.1, 22.7, 27.0, 27.2, 29.3, 29.5, 29.6, 31.9, 51.4, 75.6, 85.6, 96.7, 110.1, 110.7, 112.2, 113.9, 117.3, 122.4, 133.1, 137.0, 137.7, 153.2, 160.4, 164.3 ppm. FT-IR (KBr): ν=2923, 2852, 2214, 1604, 1484, 1467, 1418, 1346, 1300, 1210, 1184, 822, 721 cm^{-1}. MALDI-TOF-MS (dithranol): *m*/*z*: calcd for $C_{98}H_{142}Br_2N_{10}$: 1616.98 g mol^{-1}, found: 1617.9 g mol^{-1} $[MH]^+$; elemental analysis calcd (%) for $C_{98}H_{142}Br_2N_{10}$ (1616.98): C 72.66, H 8.83, N 8.56; found: C 72.68, H 8.86, N 8.58.

*4.1.5. 3,3′-(2,5-Bis((triisopropylsilyl)ethynyl)-1,4-phenylene)bis(2-(4-(dihexadecylamino)phenyl)buta-1,3-diene-1,1,4,4-tetracarbonitrile) (**2b**).* Except for the reactant monomer, all the other experiment conditions were the same as those of **2a**. The crude product was purified by column chromatography (SiO_2, CH_2Cl_2/ethyl acetate=15:1) to give **2b** (0.170 g, 93%) as a brown solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ=0.88 (m, 12H), 1.20 (m, 42H), 1.26 (s, 104H), 1.56 (m, 8H), 3.35 (m, 8H), 6.62 (d, *J*=9.3 Hz, 4H), 7.58 (s, 2H), 7.83 (d, *J*=9.2 Hz, 4H) ppm. FT-IR (KBr): ν=2924, 2853, 2213, 1604, 1483, 1466, 1345, 1212, 1184, 995, 882, 800, 724 cm^{-1}. MALDI-TOF-MS (dithranol): *m*/*z*: calcd for $C_{120}H_{184}N_{10}Si_2$: 1821.42 g mol^{-1}, found:

1822.6 g mol^{-1} $[MH]^+$; elemental analysis calcd (%) for $C_{120}H_{184}N_{10}Si_2$ (1821.42): C 79.06, H 10.17, N 7.06; found: C 79.09, H 10.16, N 7.08.

*4.1.6. 2-(1-(2,5-Dibromo-4-((4-(dihexadecylamino)phenyl)ethynyl) phenyl)-2-(4-(dicyanomethylene)cyclohexa-2,5-dienylidene)-2-(4-(dihexadecylamino)phenyl)ethylidene)malononitrile (**3a**).* Except that the click reagent was TCNQ, all the other conditions were the same as **1a**. The crude product was purified by column chromatography (SiO_2, CH_2Cl_2/ethyl acetate=15:1) to give **3a** (0.0729 g, 93%) as a brown solid. ^1H NMR ($CDCl_3$, 300 MHz): δ=0.89 (m, 12H), 1.26 (s, 104H), 1.56 (m, 8H), 3.28 (m, 4H), 3.36 (m, 4H), 6.56 (d, J=9.1 Hz, 2H), 6.62 (d, J=9.1 Hz, 2H), 7.37 (d, J=9.0 Hz, 2H), 7.13 (d, J=8.9 Hz, 2H), 7.18 (d, J=9.3 Hz, 2H), 7.23 (d, J=9.7 Hz, 2H), 7.59 (s, 1H), 7.69 (s, 1H) ppm. FT-IR (KBr): ν=2921, 2853, 2209, 1606, 1584, 1523, 1466, 1404, 1363, 1325, 1273, 1183, 1144, 1062, 959, 814, 722 cm^{-1}. MALDI-TOF-MS (dithranol): m/z: calcd for $C_{98}H_{146}Br_2N_6$: 1565.00 g mol^{-1}, found: 1566.0 g mol^{-1} $[MH]^+$; elemental analysis calcd (%) for $C_{98}H_{146}Br_2N_6$ (1565.00): C 75.06, H 9.38, N 5.36; found: C 75.10, H 9.41, N 5.38.

*4.1.7. 2-(4-(3,3-Dicyano-1-(4-(dihexadecylamino)phenyl)-2-(4-((4-(dihexadecylamino)phenyl)ethynyl)-2,5-bis((triisopropylsilyl)ethynyl)phenyl)allylidene)cyclohexa-2,5-dienylidene) malononitrile (**3b**).* Except that the click reagent was TCNQ, all the other conditions were the same as **1b**. The crude product was purified by column chromatography (SiO_2, CH_2Cl_2/ethyl acetate=10:1) to give **3b** (0.0832 g, 94%) as a green solid. ^1H NMR ($CDCl_3$, 300 MHz): δ=0.89 (m, 12H), 1.10 (m, 36H), 1.20 (m, 6H), 1.26 (s, 104H), 1.56 (m, 8H), 3.27 (m, 4H), 3.36 (m, 4H), 6.53 (d, J=9.3 Hz, 2H), 6.64 (d, J=9.3 Hz, 2H), 7.07 (s, 2H), 7.33 (d, J=9.0 Hz, 2H), 7.35 (d, J=9.3 Hz, 2H), 7.42 (d, J=9.3 Hz, 2H), 7.74 (m, 2H) ppm. FT-IR (KBr): ν=2925, 2854, 2204, 1726, 1606, 1580, 1523, 1466, 1402, 1366, 1347, 1285, 1180, 1104, 996, 883, 810, 721 cm^{-1}. MALDI-TOF-MS (dithranol): m/z: calcd for $C_{120}H_{188}N_6Si_2$: 1769.44 g mol^{-1}, found: 1770.3 g mol^{-1} $[MH]^+$; elemental analysis calcd (%) for $C_{120}H_{188}N_6Si_2$ (1769.44): C 81.38, H 10.70, N 4.75; found: C 81.40, H 10.75, N 4.76.

*4.1.8. 2,2′-(1,1′-(2,5-Dibromo-1,4-phenylene)bis(2-(4-(dicyanomethylene)cyclohexa-2,5-dienylidene)-2-(4-(dihexadecylamino)phenyl)ethan-1-yl-1-ylidene))dimalononitrile (**4a**).* Except that the click reagent was TCNQ, all the other conditions were the same as **2a**. The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate=1:3) to give **4a** (0.159 g, 90%) as an orange solid. ^1H NMR ($CDCl_3$, 300 MHz): δ=0.89 (m, 12H), 1.26 (s, 104H), 1.58 (m, 8H), 3.35 (m, 8H), 6.62 (d, J=9.2 Hz, 8H), 7.13 (d, J=9.1 Hz, 8H), 7.60 (s, 2H) ppm. FT-IR (KBr): ν=2924, 2852, 2205, 1581, 1522, 1466, 1399, 1349, 1181, 961, 862, 720 cm^{-1}. MALDI-TOF-MS (dithranol): m/z: calcd for $C_{110}H_{50}Br_2N_{10}$: 1769.04 g mol^{-1}, found: 1770.1 g mol^{-1} $[MH]^+$; elemental analysis calcd (%) for $C_{110}H_{50}Br_2N_{10}$ (1769.04): C 74.55, H 8.53, N 7.90; found: C 74.57, H 8.55, N 7.88.

*4.1.9. 3,3′-(2,5-Bis((triisopropylsilyl)ethynyl)-1,4-phenylene)bis(2-(4-(dihexadecylamino)phenyl)buta-1,3-diene-1,1,4,4-tetracarbonitrile) (**4b**).* Except for the reactant monomer, all the other experiment conditions were the same as those of 4**a**. The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate=1:4) to give **4b** (0.176 g, 89%) as a blue solid. ^1H NMR ($CDCl_3$, 300 MHz): δ=0.87 (m, 12H), 1.13 (m, 42H), 1.26 (s, 104H), 1.56 (m, 8H), 3.39 (m, 8H), 6.70 (d, J=9.6 Hz, 8H), 7.16 (s, 2H), 7.33 (d, 9.5 Hz, 4H), 7.42 (d, J=9.6 Hz) ppm. FT-IR (KBr): ν=2925, 2854, 2361, 2206, 1583, 1542, 1466, 1405, 1347, 1182, 960, 861, 799, 722 cm^{-1}. MALDI-TOF-MS (dithranol): m/z: calcd for $C_{120}H_{184}N_{10}Si_2$: 1821.42 g mol^{-1}, found: 1822.5 g mol^{-1} $[MH]^+$; elemental analysis calcd (%) for $C_{120}H_{184}N_{10}Si_2$ (1821.42): C 79.06, H 10.17, N 7.68; found: C 79.11, H 10.18, N 7.68.

*4.1.10. 2-(1-(2,5-Dibromo-4-((4-(dihexadecylamino)phenyl)ethynyl) phenyl)-2-(4-(dicyanomethylene)-2,3,5,6-tetrafluorocyclohexa-2,5-dienylidene)-2-(4-(dihexadecylamino)phenyl)ethylidene)malononitrile (**5a**).* Except that the click reagent was F_4-TCNQ, all the other conditions were the same as **1a**. The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate=1:4) to give **5a** (0.0604 g, 92%) as a green solid. ^1H NMR ($CDCl_3$, 300 MHz): δ=0.89 (m, 12H), 1.26 (s, 104H), 1.58 (m, 8H), 3.29 (m, 8H), 6.57 (d, J=9.1 Hz, 4H), 7.39 (d, J=9.0 Hz, 8H), 7.70 (s, 2H) ppm. FT-IR (KBr): ν=2923, 2852, 2198, 1633, 1599, 1568, 1523, 1467, 1431, 1387, 1356, 1308, 1190, 1143, 1066, 975, 851, 722 cm^{-1}. MALDI-TOF-MS (dithranol): m/z: calcd for $C_{98}H_{142}Br_2F_4N_6$: 1636.96 g mol^{-1}, found: 1637.9 g mol^{-1} $[MH]^+$; elemental analysis calcd (%) for $C_{98}H_{142}Br_2F_4N_6$ (1636.96): C 77.71, H 8.73, N 5.12; found: C 77.73, H 8.75, N 5.14.

*4.1.11. 2-(4-(3,3-Dicyano-1-(4-(dihexadecylamino)phenyl)-2-(4-((4-(dihexadecylamino)phenyl)ethynyl)-2,5-bis((triisopropylsilyl) ethynyl)phenyl)allylidene)-2,3,5,6-tetrafluorocyclohexa-2,5-dienylidene) malononitrile (**5b**).* Except that the click reagent was F_4-TCNQ, all the other conditions were the same as **1b**. The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate=1:3) to give **5b** (0.0578 g, 91%) as a blue solid. ^1H NMR ($CDCl_3$, 300 MHz): δ=0.87 (m, 12 H), 1.12 (m, 42H), 1.26 (s, 104H), 1.60 (m, 8H), 4.29 (m, 8H), 7.53 (d, J=6.0 Hz, 4 H), 7.54 (d, J=6.3 Hz, 4H), 7.71 (s, 2H) ppm. FT-IR (KBr): ν=2924, 2853, 2200, 1598, 1521, 1466, 1389, 1355, 1191, 1034, 970, 814, 679 cm^{-1}. MALDI-TOF-MS (dithranol): m/z: calcd for $C_{120}H_{184}F_4N_6Si_2$: 1841.41 g mol^{-1}, found: 1842.5 g mol^{-1} $[MH]^+$; elemental analysis calcd (%) for $C_{120}H_{184}F_4N_6Si_2$ (1841.41): C 78.21, H 10.06, N 4.56; found: C 78.23, H 10.07, N 4.55.

*4.1.12. 2,2′-(1,1′-(2,5-Dibromo-1,4-phenylene)bis(2-(4-(dicyanomethylene)-2,3,5,6-tetrafluorocyclohexa-2,5-dienylidene)-2-(4-(dihexadecylamino)phenyl)ethan-1-yl-1-ylidene))dimalononitrile (**6a**).* Except that the click reagent was F_4-TCNQ, all the other conditions were the same as **2a**. The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate=1:2) to give **6a** (0.174 g, 91%) as a red solid. ^1H NMR ($CDCl_3$, 300 MHz): δ=0.89 (m, 12H), 1.26 (s, 104H), 1.57 (m, 8H), 3.29 (m, 8H), 6.57 (d, J=9.2 Hz, 4H), 7.69 (s, 2H) ppm. FT-IR (KBr): ν=2924, 2853, 2198, 1633, 1598, 1526, 1484, 1389, 1356, 1192, 1039, 975, 822, 777 cm^{-1}. MALDI-TOF-MS (dithranol): m/z: calcd for $C_{110}H_{142}Br_2F_8N_{10}$: 1912.97 g mol^{-1}, found: 1913.8 g mol^{-1} $[MH]^+$; elemental analysis calcd (%) for $C_{110}H_{142}Br_2F_8N_{10}$ (1912.97): C 65.95, H 7.47, N 7.31; found: C 66.98, H 7.47, N 7.32.

*4.1.13. 2,2′-(1,1′-(2,5-Bis((triisopropylsilyl)ethynyl)-1,4-phenylene) bis(2-(4-(dicyanomethylene)-2,3,5,6-tetra-fluorocyclohexa-2,5-dienylidene)-2-(4-(dihexadecylamino)phenyl)ethan-1-yl-1-ylidene)) dimalononitrile (**6b**).* Except that the click reagent was F_4-TCNQ, all the other conditions were the same as **2b**. The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate=1:2) to give **6b** (0.195 g, 92%) as an orange solid. ^1H NMR ($CDCl_3$, 300 MHz): δ=0.87 (m, 12 H), 1.13 (m, 42H), 1.26 (s, 104H), 1.56 (m, 8H), 3.39 (m, 8H) ppm. FT-IR (KBr): ν=2925, 2853, 2200, 1635, 1599, 1533, 1483, 1389, 1352, 1311, 1192, 1038, 974, 882, 820, 723 cm^{-1}. MALDI-TOF-MS (dithranol): m/z: calcd for $C_{132}H_{184}F_8N_{10}Si_2$: 2117.41 g mol^{-1}, found: 2118.5 g mol^{-1} $[MH]^+$; elemental analysis calcd (%) for $C_{132}H_{184}F_8N_{10}Si_2$ (2117.41): C 74.82, H 8.75, N 6.61; found: C 74.84, H 8.76, N 6.62.

*4.1.14. 2-(4-(Dihexadecylamino)phenyl)-3-(4-((4-nitrophenyl) ethynyl)phenyl)buta-1,3-diene-1,1,4,4-tetracarbonitrile (**7a**).* Except for

the reactant monomer, all the other experiment conditions were the same as those of **1a**. The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate=1:1) to give **7a** (0.0976 g, 91%) as a purple solid. ^1H NMR ($CDCl_3$, 300 MHz): δ=0.88 (m, 6H), 1.25 (s, 52H), 1.58 (m, 4H), 3.38 (m, 4H), 6.67 (d, J=9.6 Hz, 2H), 7.66 (d, J=9.3 Hz, 2H), 7.71 (s, 1H), 7.74 (m, 2H), 7.92 (s, 1H), 8.26 (m, 2H) ppm. FT-IR (KBr): ν=2924, 2852, 2215, 1603, 1521, 1484, 1466, 1417, 1342, 1289, 1208, 1183, 1063, 856, 822, 749 cm^{-1}. MALDI-TOF-MS (dithranol): m/z: calcd for $C_{60}H_{78}N_6O_2$: 914.62 g mol^{-1}, found: 915.6 g mol^{-1} $[MH]^+$; elemental analysis calcd (%) for $C_{60}H_{78}N_6O_2$ (914.62): C 78.73, H 8.59, N 9.18; found: C 78.72, H 8.56, N 9.16.

*4.1.15. 2-(2,5-Dibromo-4-((4-(hexadecyloxy)phenyl)ethynyl)phenyl)-3-(4-(dihexadecylamino)phenyl)buta-1,3-diene-1,1,4,4-tetracarbonitrile (**8a**).* Except for the reactant monomer, all the other experiment conditions were the same as those of **1a**. The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate=1:1) to give **8a** (0.114 g, 90%) as an orange solid. ^1H NMR ($CDCl_3$, 300 MHz): δ=0.88 (m, 9H), 1.25 (s, 78H), 1.62 (m, 4H), 1.79 (m, 2H), 3.37 (m, 4H), 3.98 (m, 2H), 6.65 (d, J=9.6 Hz, 2H), 6.89 (m, 2H), 7.50 (m, 2H), 7.65 (d, J=9.3 Hz, 2H), 7.75_4 (s, 1H), 7.84 (s, 1H) ppm. FT-IR (KBr): ν=2923, 2852, 2215, 1603, 1574, 1519, 1489, 1467, 1416, 1341, 1291, 1252, 1183, 1061, 832 cm^{-1}. MALDI-TOF-MS (dithranol): m/z: calcd for $C_{76}H_{109}Br_2N_5O$: 1265.70 g mol^{-1}, found: 1266.8 g mol^{-1} $[MH]^+$; elemental analysis calcd (%) for $C_{76}H_{109}Br_2N_5O$ (1265.70): C 71.96, H 8.66, N 5.52; found: C 72.01, H 8.68, N 5.53.

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Supplementary data

Cyclic voltammograms and UV–vis spectra of products **1a**–**8a**, **1b**–**6b** and reactants **C1**–**C4**. Supplementary data related to this article can be found online at http://dx.doi.org/10.1016/j.tet.2012.10.081.

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