

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/50849104>

N -Arylpyrrole-Based Chromophores of Donor- π -Donor Type Displaying High Two-Photon Absorption

ARTICLE in THE JOURNAL OF PHYSICAL CHEMISTRY B · MARCH 2011

Impact Factor: 3.3 · DOI: 10.1021/jp111919z · Source: PubMed

CITATIONS

8

READS

11

10 AUTHORS, INCLUDING:



Qianqian Li

Wuhan University

73 PUBLICATIONS 2,026 CITATIONS

SEE PROFILE



Cheng Zhong

Wuhan University

89 PUBLICATIONS 2,028 CITATIONS

SEE PROFILE



Jingui Qin

Wuhan University

480 PUBLICATIONS 10,779 CITATIONS

SEE PROFILE



Zhen Li

Wuhan University

352 PUBLICATIONS 9,469 CITATIONS

SEE PROFILE

N-Arylpyrrole-Based Chromophores of Donor- π -Donor Type Displaying High Two-Photon Absorption

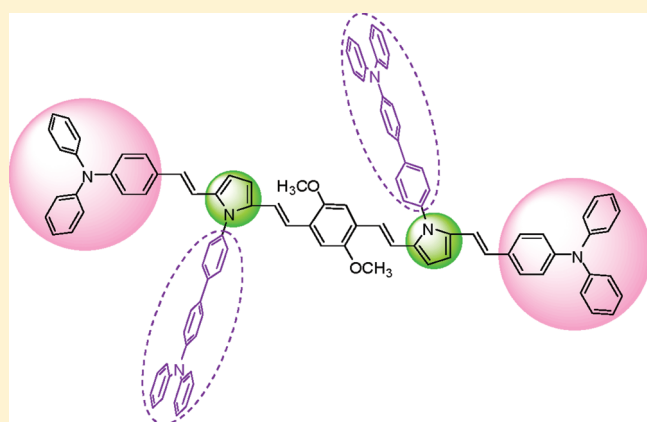
Qianqian Li,[†] Jing Huang,[†] Aoshu Zhong,[†] Cheng Zhong,[†] Ming Peng,[†] Jun Liu,[‡] Zhiguo Pei,[‡] Zhenli Huang,[‡] Jingui Qin,[†] and Zhen Li^{*,†}

[†]Department of Chemistry, Hubei Key Laboratory on Organic and Polymeric Opto-Electronic Materials, Wuhan University, 430072, People's Republic of China

[‡]Key Laboratory of Biomedical Photonics of Ministry of Education, Huazhong University of Science and Technology, 430074, People's Republic of China

Supporting Information

ABSTRACT: A series of new *N*-arylpyrrole-based chromophores with the donor- π -donor structure have been designed and synthesized via Wittig–Horner–Emmons olefination and Suzuki coupling reactions. The electronic and optical properties of the designed chromophores could be well tuned by modifying the conjugation bridges and changing the groups linked to the pyrrole moieties through the C–N single bond. All the chromophores exhibited two-photon absorption activity in the range of 730–900 nm with a large two-photon absorption cross section (~ 1000 – 1700 GM).



INTRODUCTION

Organic molecules displaying high two-photon absorption (2PA) properties have received increasing attention, owing to their potential applications in three-dimensional (3-D) fluorescence imaging, optical power limitation, lasing up-conversion, 3-D optical data storage, 3-D microfabrication, and photodynamic therapy.^{1–3} To fully exploit the great potential of the 2PA process, the design and synthesis of molecules with large two-photon absorption cross sections (σ) are still ongoing, and a certain part of the structure–property relationships has been investigated.^{4,5} In particular, extended π -conjugated systems symmetrically substituted with electron-donating (D) and/or electron-accepting (A) functionalities have been revealed as efficient 2PA molecules, which exhibited two-photon absorption cross sections at least 1 order of magnitude larger than the corresponding unsubstituted molecules, indicating that the efficient intramolecular charge transfer (ICT) made by the donating and/or withdrawing abilities of the electron donor and/or acceptor played an important role in increasing their σ values.^{6,7} Thus, different constructing blocks with different donating or withdrawing abilities would affect the 2PA properties in a large degree. So far, a large number of 2PA chromophores with substituted aromatic rings as the conjugated bridges have been explored, with organic simple functionalities such as OR, NR₂, NO₂, and CN on them. As a result, the electronic properties of

the whole chromophores could be well tuned. Moreover, the replacement of the aromatic systems with more easily delocalizable π -excessive or π -deficient heteroaromatic led to increased ICT as well as an enhanced two-photon absorption.^{8,9} Furthermore, the intrinsic tunable nature of the heteroaromatic rings made these systems particularly appropriate for the fine control of their electronic and optical properties. For example, the recent employment of heterocycles, such as thiophene, pyrrole, or carbazole, in the design of novel chromophores with enhanced 2PA properties has already been reported.¹⁰

As one of the strongest donor heteroaromatics, pyrrole demonstrated attractive chemical and physical properties, making it a good building block for the construction of 2PA chromophores. By incorporating the electron-rich pyrrole ring as the auxiliary donor to the various types of chromophores, large two-photon absorption cross sections have been reported by Marder and co-workers.¹¹ Other different types of pyrrole-containing chromophores, including D- π -A, D-A-D, and D- π -D types, also exhibited good performance. In almost all the reported pyrrole-containing chromophores, the pyrrole moieties were functionalized at the α -position to build the conjugated

Received: December 15, 2010

Revised: February 1, 2011

Published: March 24, 2011

2PA molecules, with the full utilization of this special heteroaromatic ring as an efficient π -center or an auxiliary donor. Interestingly, some alkyl groups were linked to the nitrogen atoms in the pyrrole rings (*N*-alkylpyrrole), possibly to improve the solubility of the resultant chromophores. However, it seemed that there were no reports concerning the 2PA chromophores with *N*-arylpyrrole moieties, although it should be a useful approach to modify the electronic properties of the pyrrole-containing chromophores through the introduction of some aromatic groups to the nitrogen atoms in the pyrrole ring.

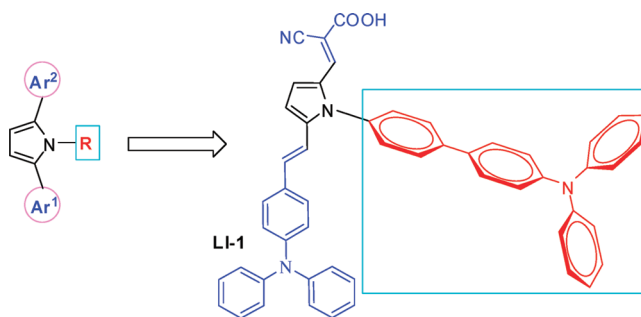
Recently, we attempted to link some aromatic moieties to the nitrogen atom in the pyrrole ring to design some new pyrrole-based functional molecules, and we studied their properties in details. The obtained experimental results demonstrated that *N*-arylpyrrole acting as the building block could efficiently enhance the stability of the resultant chromophores in comparison with that of the *N*-alkylpyrrole-based analogues. Interestingly, their performance could be adjusted in some degree.¹² For examples, as shown in Chart 1, when *N*-arylpyrrole moieties were introduced into the dye sensitizers as π -bridge (LI-1), a high conversion efficiency of 7.21% was achieved in its corresponding solar-cell devices, which was 91% of the standard cell from N719 tested under similar conditions.^{12a} Prompted by these exciting results, in this paper, we further designed some 2PA chromophores of the D- π -D type (Scheme 1, PL-1–4), in which triphenylamine acted as the electron donor and the fluorenylene or the phenylene unit and *N*-arylpyrrole as the π -conjugated bridge. The 2PA spectra of chromophores were obtained over a broad spectral range by a two-photoinduced fluorescence technique, and chromophore PL-3 gave the highest σ value of 1716 GM at 760 nm. Herein, we report the synthesis and characterization, by linear optical absorption and fluorescence, as well as the 2PA properties of four *N*-arylpyrrole-based two-photon absorption chromophores.

EXPERIMENTAL SECTION

Materials. Tetrahydrofuran (THF) was dried over and distilled from a K–Na alloy under an atmosphere of dry argon. Compounds 1–3 were prepared according to the literature.^{12–14} All other reagents were used as received.

Instrumentation. ¹H and ¹³C NMR spectra were measured on a Varian Mercury300 spectrometer using tetramethylsilane (TMS; δ = 0 ppm) as internal standard. The Fourier transform infrared (FTIR) spectra were recorded on a Perkin-Elmer-2 spectrometer in the region of 3000–400 cm^{−1}. UV–visible spectra were obtained on a Shimadzu UV-2550 spectrometer. Photoluminescence spectra were performed on a Hitachi F-4500 fluorescence spectrophotometer. Matrix-assisted laser desorption ionization time-of-flight mass spectra were measured on a Voyager-DESTR MALDI-TOF mass spectrometer (MALDI-TOF MS; ABI, American) equipped with a 337 nm nitrogen laser and a 1.2 m linear flight path in positive ion mode. Elemental analyses were performed on a Carloerba-1106 microelemental analyzer. Thermal analysis was performed on a Netzsch STA449C thermal analyzer at a heating rate of 10 °C/min in argon at a flow rate of 50 cm³/min for thermogravimetric analysis (TGA). The thermometer for measurement of melting points was uncorrected. Electrochemical cyclic voltammetry was conducted on a Zahner IM6e Electrochemical Workstation with Pt disk, Pt plate, and Ag/Ag⁺ electrode as working electrode, counterelectrode, and reference electrode, respectively, in a 0.1

Chart 1



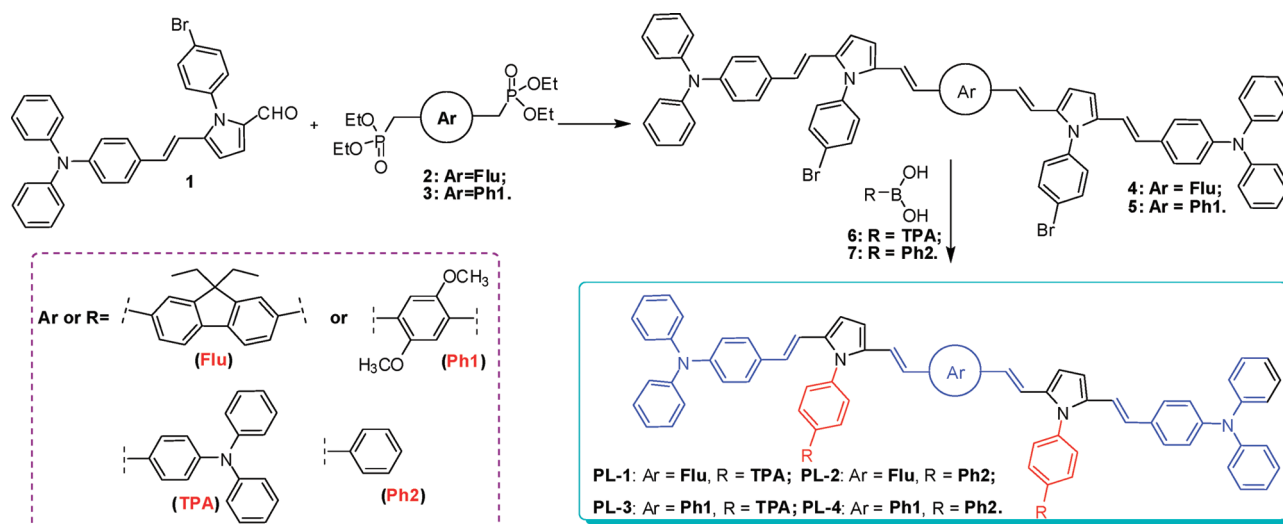
mol/L tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) acetonitrile solution. A mode-locked Ti:sapphire laser (Mai Tai, Spectra-Physics Inc.) was used as the excitation source. The average output power, pulse width, and repetition rate were 1.5 W, 100 fs, and 80 MHz, respectively. After passing through a circular variable neutral density filter that was used to control the power of the laser, the laser was focused into the cell (polished on all sides) by a focusing lens (f = 6 cm). The emission light was collected by an objective lens (10 \times , NA = 0.3, Olympus, Japan) and then was focused by another objective lens (10 \times , NA = 0.25, DHC, China) into a fiber optic spectrometer (USB2000+, Ocean Optics Inc.), which was used to record the fluorescent spectra. An aqueous solution of fluorescein (pH = 11) was chosen as the reference standard.

Synthesis of Compounds 4 and 5. Compound 2 (0.38 g, 0.73 mmol) was suspended in 20 mL of anhydrous tetrahydrofuran under an atmosphere of dry argon. *t*-BuOK (0.33 g, 2.93 mmol) was added directly as a solid, and the resultant mixture was stirred at room temperature for 10 min. After the addition of the solution of compound 1 (0.80 g, 1.54 mmol) in anhydrous tetrahydrofuran (10 mL) dropwise, the reaction mixture was stirred at room temperature overnight and then poured into 100 mL of water. The organic product was extracted with chloroform and dried over anhydrous Na₂SO₄. After removal of the solvent, the crude product was purified through a silica gel chromatography column by use of petroleum/ethyl acetate (10/1) as eluent to afford an orange solid 4 (0.69 g, 75.4%). Mp: 81–82 °C. ¹H NMR (CDCl₃) δ (ppm): 7.71–7.38 (m, 10 H, ArH), 7.27–6.96 (m, 32 H, ArH and –CH=CH–), 6.89–6.55 (m, 32 H, ArH and –CH=CH–), 6.43 (d, 2H, J = 16.5 Hz, –CH=CH–).

Compound 5 was prepared from compound 3 instead of 2 by following a similar procedure. The crude product was purified through a silica gel chromatography column by use of petroleum/ethyl acetate (10/1) as eluent to afford a red solid 5 (0.86 g, 52.5%). Mp: 155–156 °C. ¹H NMR (CDCl₃) δ (ppm): 7.67–7.64 (m, 4H, ArH), 7.57 (d, 2H, J = 8.4 Hz, ArH), 7.22 (d, 6H, J = 7.5 Hz, ArH), 7.16–6.95 (m, 26H, ArH and –CH=CH–), 6.82–6.57 (m, 10H, ArH), 6.46–6.40 (m, 2H, –CH=CH–), 3.87–3.70 (m, 6H, –OCH₃).

General Procedure for Synthesis of Compounds PL-1–4. A mixture of compound 4 or 5 (1 equiv), 4-(diphenylamino)phenylboronic acid or phenylboronic acid (3 equiv), sodium carbonate (20 equiv), and a catalytic amount of tetrakis(triphenylphosphine)palladium [Pd(PPh₃)₄] was carefully degassed and charged with argon. Subsequently, THF and deoxidized water were added by syringe. The reaction mixture

Scheme 1



was stirred at 80 °C for 48 h. After the mixture was cooled to room temperature, the organic layer was separated, dried over sodium sulfate, and evaporated to dryness. The crude product was purified by column chromatography on silica gel.

Compound PL-1 was prepared from **4** (200 mg, 0.16 mmol) and 4-(diphenylamino)phenylboronic acid (139 mg, 0.48 mmol): orange solid (150 mg, 59.4%), mp 187–188 °C. ^1H NMR (CDCl_3) δ (ppm): 7.75 (d, 2H, J = 7.5 Hz, ArH), 7.65 (d, 2H, J = 7.8 Hz, ArH), 7.59 (d, 2H, J = 6.6 Hz, ArH), 7.51 (d, 4H, J = 7.5 Hz, ArH), 7.43 (d, 6H, J = 9.6 Hz, ArH), 7.31–7.20 (m, 12H, ArH), 7.16–7.12 (m, 18H, ArH), 7.08–6.92 (m, 26H, ArH and $-\text{CH}=\text{CH}-$), 6.83 (d, 4H, J = 18.9 Hz, $-\text{CH}=\text{CH}-$), 6.70–6.68 (m, 4H, ArH), 6.54 (d, 2H, J = 15.3 Hz, $-\text{CH}=\text{CH}-$), 2.05 (br s, 4H, $-\text{CH}_2-$), 0.40–0.32 (m, 6H, $-\text{CH}_3$). ^{13}C NMR (CDCl_3) δ (ppm): 150.8, 147.8, 147.4, 139.7, 130.5, 129.5, 127.9, 127.5, 127.2, 127.0, 126.3, 124.8, 124.7, 124.5, 124.0, 123.8, 123.3, 123.1, 121.0, 119.9, 116.5, 107.3, 56.1, 33.0, 8.9. MS (MALDI-TOF): m/z calcd for $\text{C}_{117}\text{H}_{92}\text{N}_6$ [M^+], 1581.7417; found, 1581.3287.

Compound PL-2 was prepared from **4** (200 mg, 0.16 mmol) and phenylboronic acid (58.5 mg, 0.48 mmol): orange solid (101 mg, 50.5%), mp 157–158 °C. ^1H NMR (CDCl_3) δ (ppm): 7.79–7.75 (m, 2H, ArH), 7.71–7.57 (m, 6H, ArH), 7.53–7.37 (m, 12H, ArH), 7.26–7.16 (m, 14H, ArH), 7.11–6.85 (m, 20H, ArH and $-\text{CH}=\text{CH}-$), 6.74–6.60 (m, 8H, ArH), 6.54 (d, 2H, J = 16.2 Hz, $-\text{CH}=\text{CH}-$), 2.01–1.92 (m, 4H, $-\text{CH}_2-$), 0.43–0.26 (m, 4H, $-\text{CH}_3$). ^{13}C NMR (CDCl_3) δ (ppm): 150.9, 147.8, 147.4, 146.9, 141.4, 140.6, 140.4, 140.3, 140.2, 136.8, 135.0, 134.8, 132.3, 130.7, 130.5, 129.6, 129.5, 129.2, 128.1, 127.9, 127.4, 127.3, 127.2, 127.0, 126.8, 126.7, 126.3, 125.7, 124.9, 124.7, 124.6, 123.9, 123.8, 123.5, 123.3, 123.1, 121.6, 121.1, 119.9, 119.8, 117.1, 116.4, 108.2, 107.9, 107.4, 77.5, 77.3, 77.1, 56.1, 33.0, 8.8. MS (MALDI-TOF): m/z calcd for [M^+], 1246.5913; found, 1246.5010. Anal. Calcd for $\text{C}_{93}\text{H}_{74}\text{N}_4$: C, 89.53; H, 5.98; N, 4.49. Found: C, 89.98; H, 6.01; N, 4.35.

Compound PL-3 was prepared from **5** (200 mg, 0.17 mmol) and 4-(diphenylamino)phenylboronic acid (139 mg, 0.48 mmol): red solid (120 mg, 47.2%), mp 168–169 °C. ^1H NMR (CDCl_3) δ (ppm): 7.71–7.61 (m, 6H, ArH), 7.55–7.49 (m, 6H, ArH), 7.41–7.35 (m, 8H, ArH), 7.31–7.20 (m, 12H, ArH), 7.15

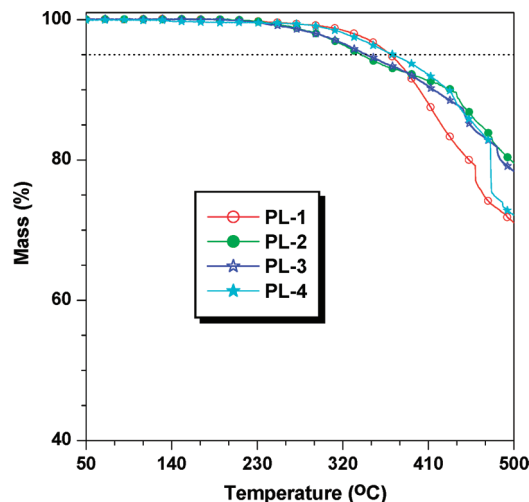


Figure 1. TGA thermograms of chromophores measured in argon at a heating rate of 10 °C/min.

(d, 14H, J = 7.2 Hz, ArH), 7.06 (d, 14H, J = 7.2 Hz, ArH), 6.99–6.93 (m, 10H, ArH), 6.69 (d, 8H, J = 13.8 Hz, $-\text{CH}=\text{CH}-$), 3.83–3.65 (m, 6H, $-\text{OCH}_3$). ^{13}C NMR (CDCl_3) δ (ppm): 151.7, 147.8, 147.3, 146.9, 140.8, 135.3, 135.0, 133.8, 132.4, 130.3, 129.6, 129.4, 128.0, 127.5, 127.3, 127.1, 126.9, 126.3, 125.6, 124.8, 124.7, 124.5, 123.9, 123.4, 123.1, 120.9, 118.4, 116.6, 109.7, 108.4, 107.9, 56.8, 56.6. MS (MALDI-TOF): m/z calcd for [$\text{M} + 1$] $^+$, 1497.6656; found, 1497.5856.

Compound PL-4 was prepared from **5** (200 mg, 0.17 mmol) and phenylboronic acid (58.5 mg, 0.48 mmol): red solid (105 mg, 53.1%), mp 149–150 °C. ^1H NMR (CDCl_3) δ (ppm): 7.77–7.62 (m, 12H, ArH), 7.49–7.38 (m, 12H, ArH), 7.21 (d, 8H, J = 7.2 Hz, ArH), 7.10–6.93 (m, 20H, ArH), 6.69 (d, 8H, J = 10.2 Hz, $-\text{CH}=\text{CH}-$), 3.89–3.64 (m, 6H, $-\text{OCH}_3$). ^{13}C NMR (CDCl_3) δ (ppm): 146.8, 143.0, 142.6, 142.1, 136.6, 135.5, 132.2, 131.7, 130.6, 130.5, 130.2, 127.6, 127.4, 125.7, 124.9, 124.8, 124.7, 124.5, 124.4, 123.4, 123.2, 122.6, 122.5, 122.4, 122.2, 121.5, 120.0, 119.8, 119.2, 119.0, 118.5, 118.3, 116.4, 113.6, 111.7, 105.0, 103.6, 103.1, 102.5, 51.8. MS (MALDI-TOF): m/z calcd for [M^+], 1162.5186;

Table 1. Some Characterization Data of Chromophores

	$\lambda_{\text{max}}^{\text{ab}}$ ^a (nm)	$\lambda_{\text{max}}^{\text{ab}}$ ^b (nm)	$\lambda_{\text{max}}^{\text{em}}$ ^c (nm)	$\lambda_{\text{max}}^{\text{em}}$ ^d (nm)	$\lambda_{\text{max}}^{\text{ip}}$ ^e (nm)	E_{ox}^{f} (V)	HOMO ^g (eV)	LUMO ^g (eV)	Φ^{h} (%)	σ^{i} (GM)	T_{d}^{j} (°C)
PL-1	447 (5.6×10^4)	440	517	540	760	0.30	−5.01	−2.60	62.4	1354	369
PL-2	452 (7.7×10^4)	460	523	550	760	0.29	−5.00	−2.59	66.3	1042	340
PL-3	469 (6.7×10^4)	482	554	592	760	0.15	−4.86	−2.60	41.0	1716	345
PL-4	469 (9.1×10^4)	480	551	588	760	0.14	−4.85	−2.60	38.2	1484	373

^a 1.0×10^{-6} M in THF, wavelength of maximum absorbance; the value of molar absorptivity (ϵ , $\text{cm}^{-1} \cdot \text{mol}^{-1} \cdot \text{L}$) is given in parentheses. ^b Absorption spectra of chromophores in thin film, wavelength of maximum absorbance. ^c 1.0×10^{-6} M in THF, wavelength of maximum intensity. ^d PL spectra of chromophores in thin film, wavelength of maximum intensity. ^e 2.0×10^{-5} M in THF, wavelength of maximum 2PA cross sections. ^f Estimated from the onset oxidation potential. ^g HOMO = $-(E_{\text{ox}}^{\text{onset}} + 4.71)$ eV, LUMO = $E_{\text{g}}^{\text{opt}} + \text{HOMO}$, The optical band gap ($E_{\text{g}}^{\text{opt}}$) was obtained from the empirical formula $E_{\text{g}} = 1240/\lambda_{\text{edge}}$. ^h Quantum yields in THF solution with fluorescein in water ($\Phi = 90\%$, pH = 11) as a standard. ⁱ 2PA cross sections, 1 GM (Göppert–Mayer) = $10^{-50} \text{ cm}^4 \cdot \text{s} \cdot \text{photon}^{-1}$; the experimental uncertainty on σ_{max} is on the order of 10–15%. ^j The 5% weight loss temperature of chromophores detected by the TGA analyses under argon at a heating rate of 10 °C/min.

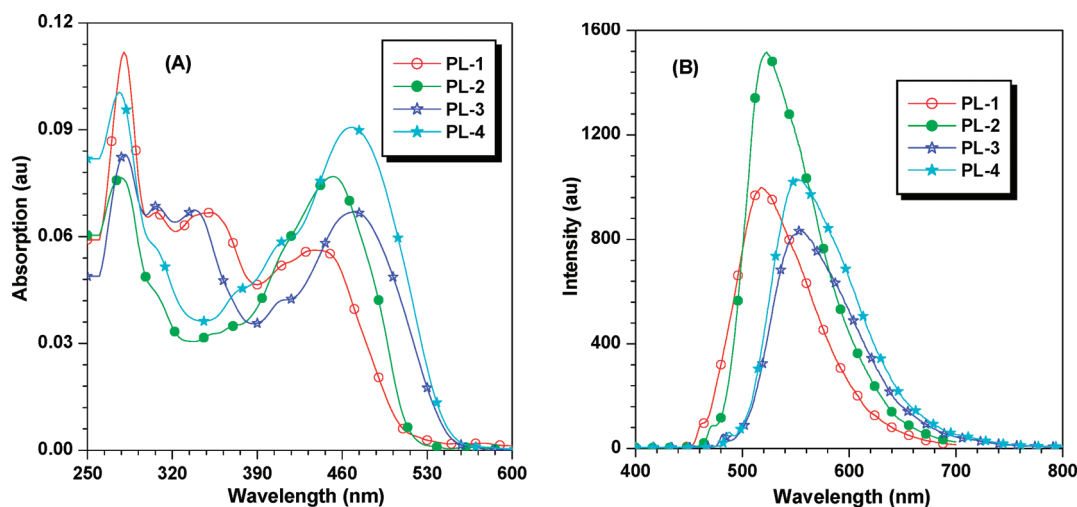


Figure 2. UV–vis spectra of chromophores in THF (left) and photoluminescence spectra of chromophores in THF (right). Concentration: 1.0 μM .

found: 1162.2011. Anal. Calcd for $\text{C}_{84}\text{H}_{66}\text{N}_4\text{O}_2$: C, 86.72; H, 5.72; N, 4.82. Found: C, 86.20; H, 5.90; N, 4.52.

RESULTS AND DISCUSSION

Synthesis and Characterization. The synthetic route for 2PA chromophores is outlined in Scheme 1. The conjugation skeletons were easily synthesized through the Wittig–Horner–Emmons olefination of aldehyde 1 and the required bisphosphonates in the presence of *t*-BuOK in THF, with satisfactory yields from 52.5% to 75.4%. By utilizing this approach, the aromatic ethylene derivatives were chosen to tune the conjugation ability of the π -bridge and the electronic properties of the whole molecules. Finally, the chromophores were obtained by the palladium-catalyzed Suzuki coupling of compound 4 or 5 with different aromatic borates. In this step, triphenylamine and phenyl were linked with *N*-phenylpyrrole for adjusting the electronic properties of the chromophores.

All the chromophores were soluble in common organic solvents, such as THF, chloroform, *N,N*-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO). They were characterized by ^1H and ^{13}C NMR and MALDI-TOF mass spectrometry (seen in the Supporting Information). The thermal behaviors of these chromophores were measured by TGA under argon, and all of them exhibited very good thermal stability with the initial decomposition temperature higher than 340 °C (over 95% of their mass retained, Figure 1). Detailed data are shown in Table 1.

One-Photon Physical Properties. Figure 2 shows representative examples of UV–vis absorption spectra of the chromophores measured in THF at a concentration of 1.0 μM , with the corresponding data summarized in Table 1. All the chromophores show a broad and intense absorption band ($\epsilon = 56\,000$ – $91\,000 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$) with maximum absorption wavelengths in the range of 440–470 nm, which should be ascribed to the efficient ICT between the donor and the π -bridge. PL-1 and PL-2 exhibited similar absorption maximum wavelengths. Interestingly, the maximum absorption wavelengths of PL-3 and PL-4 were the same. It suggested that the aromatic rings linked to pyrrole through the C–N single bond have little effect on the absorption maximum, but the peak (~ 340 nm) in the absorption spectra of PL-1 and PL-3 might be attributed to the weak effect of the triphenylamine group, which was linked to pyrrole together with phenyl one through the C–N single bond as an auxiliary donor group. That is to say, the spectra in the range of 300–400 nm could be tuned by the linkage of different R^2 groups, providing another approach to subtly modify the electronic properties of the resultant chromophores. PL-3 and PL-4 exhibited a red shift of about 20 nm in comparison with PL-1 and PL-2, indicating the presence of the electron-donating effect of bismethoxy groups in the phenylene units.

Photoluminescence spectra of chromophores, measured in THF solutions, exhibited a single peak, indicating that the emission occurs from the lowest excited state with the largest

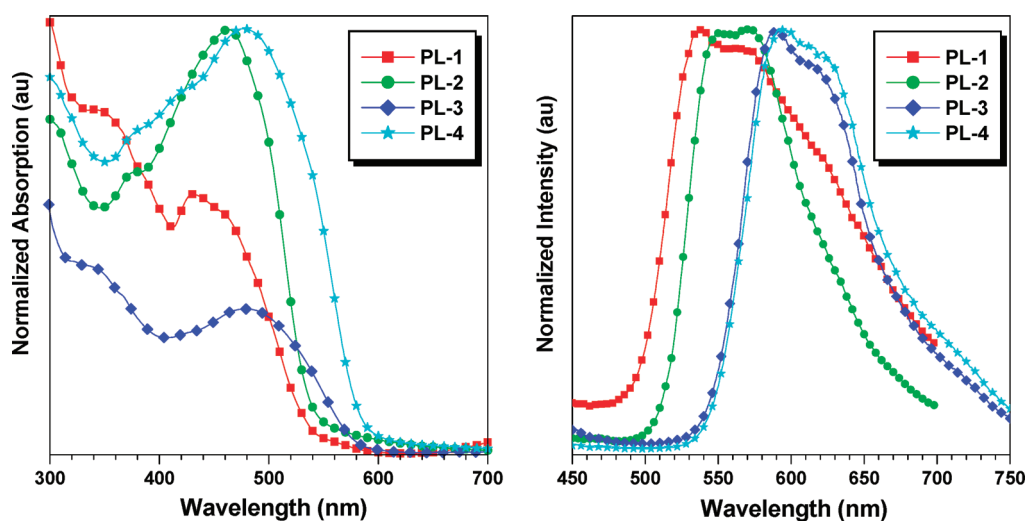


Figure 3. Normalized solid-state absorption spectra (left) and normalized solid-state photoluminescence spectra (right) of the chromophores.

oscillator strength (Figure 2). PL-1 and PL-2 emitted strong luminescence with maximum emission wavelengths at about 520 nm, while those of PL-3 and PL-4 occurred at about 550 nm. The replacement of a fluorenylene unit by a 1,4-dimethoxyphenylene unit resulted in a red shift of 30 nm, and the fluorescent color turned from green to yellow. The different emission behavior was similar to the difference in their UV-vis spectra. Thus, the same trend indicates that the electron-donating effect of bismethoxy groups played the dominant role, though the fluorenylene unit possessed the larger conjugation space. This was not so strange. In our previous work, similar phenomena were observed when bismethoxy groups were used instead of the fluorenylene unit.^{12d} Really, in comparison with the bismethoxy groups, the fluorenylene unit exhibited a longer conjugation length. However, the electronic and photonic properties of the prepared molecules were determined by the whole molecules, including the different constructing blocks and the communications among them. Perhaps the latter was more important here. Possibly, it might be much easier for the bismethoxy groups to communicate with other moieties here in PL-3 and PL-4 than the fluorenylene unit, since the well-formed stable large π system in the fluorenylene unit could hamper its communication with other aromatic rings to some degree. The quantum yields were tested to be in the range of 0.38–0.66; the smaller quantum yields of PL-3 and PL-4 should be caused by the much lower energy of the emitting states, which might facilitate nonradiative pathways.

Figure 3 shows the optical properties of these chromophores in the solid state, with the corresponding data summarized in Table 1. The trend of the solid-state spectra was similar to the solution spectra; however, the spectra were red-shifted to different degrees. Generally, the conjugated systems became more planar in the solid state, which led to an increase in the effective conjugation length and the red-shifted absorption and photoluminescence spectra in comparison with those in solutions. As the conjugated bridges and aromatic rings linked to the pyrrole ring were different, the intermolecular interactions of the four chromophores were not the same, thus resulting in the different degrees of red shifts.

Furthermore, density functional theory (DFT) calculations were performed at the B3LYP/6-31G(d) level by use of the

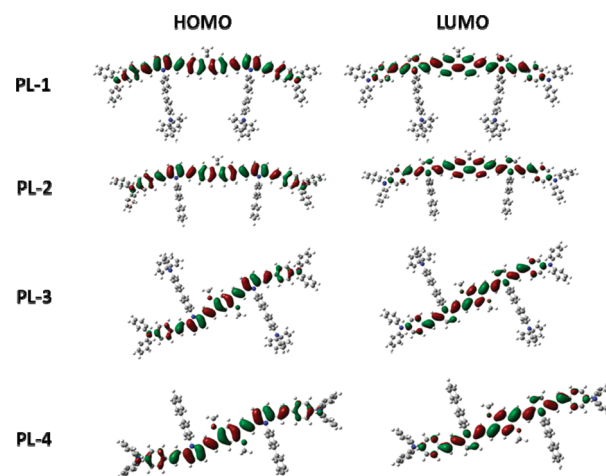


Figure 4. Frontier orbitals of chromophores PL-1–4.

Gaussian 03 program,¹⁵ and the corresponding Kohn–Sham orbitals were obtained at the same level of theory. To simplify the calculating process, aliphatic side chains in PL-1 and PL-2 were replaced by methyl groups. This is a reasonable approach since the substituents in the 9-position of the fluorene ring were not in conjugation with the aromatic system and had no noticeable effect on the electronic distribution or photophysical properties of the chromophore system. The calculated frontier orbitals for chromophores are shown in Figure 4. The optimized structures possessed a high degree of coplanarity, which should be a beneficial factor for communication between the donor and conjugated bridge, hence favoring the enhancement of the two-photon absorption cross sections.

Electrochemical Properties. Cyclic voltametry (CV) was employed to investigate the redox behavior of the chromophores and estimate their highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels. The CV curves are shown in Figure 5 and the corresponding data are summarized in Table 1. All reported potentials were calibrated against the ferrocene/ferrocenium (Fc/Fc^+) couple, which was used as the internal standard. In the anodic scan, the initial onset oxidation potential of the chromophores was

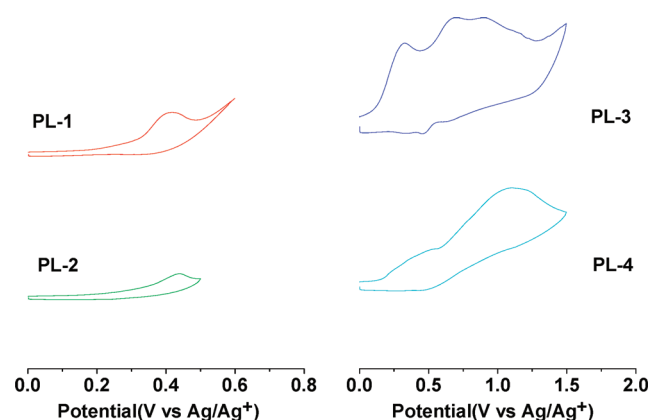


Figure 5. Cyclic voltammograms of chromophores on platinum electrode in 0.1 mol/L Bu_4NPF_6 , CH_3CN solution with a scan rate of 100 mV/s.

found to occur at 0.30, 0.29, 0.15, and 0.14 V (vs Ag/Ag^+), which corresponded to HOMO levels of -5.01 , -5.00 , -4.86 , and -4.85 eV, respectively, according to the empirical equation $E_{(\text{HOMO})} = -(E_{\text{ox}} + 4.71)$. Since the cathodic scans for these chromophores failed despite many attempts, their LUMO energies were estimated from the optical band gaps and the HOMO energies. As a result of the electron-donating effect of bismethoxy groups in the phenylene unit mentioned above, PL-3 and PL-4 exhibited relatively higher HOMO levels, in comparison with PL-1 and PL-2 with fluorenylene unit as the core. And the groups linked to pyrrole moieties through C—N single bond have little effect on the electrochemical properties.

Two-Photon Absorption Properties. The two-photon absorption cross sections of chromophores in THF at a concentration of 2×10^{-5} M were measured by the two-photon induced fluorescence technique, using femtosecond laser pulses, ranging from 730 to 900 nm. In all cases, the output intensity of two-photon excited fluorescence was linearly dependent on the square of the input laser intensity, thereby confirming the 2PA process. The σ values were calculated according to the following equation:

$$\sigma_{2s} = \frac{F_s}{F_r} \frac{\Phi_r n_r c_r}{\Phi_s n_s c_s} \sigma_{2r}$$

The subscripts s and r stand for the measured sample and reference molecule, respectively; F is the integrated fluorescence intensity measured at the same power as the excitation beam; Φ is the fluorescence quantum yield; and c is the number density of the molecules in the solution. σ_{2r} is termed as the 2PA cross section of the reference molecule. Here, fluorescein was chosen as the reference molecule.

All the chromophores were stable under the test conditions, and no obvious change was observed in the UV–vis spectra after completion of the 2PA measurements. The 2PA spectra of the chromophores are shown in Figure 6, with the data summarized in Table 1. The maximum values of the 2PA cross sections for the chromophores occur at 760 nm, which was less than twice that of the single photo absorption, proving a quadrupolar character. Upon comparison of the two series, chromophores with fluorenylene or 1,4-dimethoxyphenylene unit as the conjugated bridge, the σ values of the latter were higher than those of the former. This was reasonable: the two methoxy groups substituted on the phenyl ring increased the electron density of the

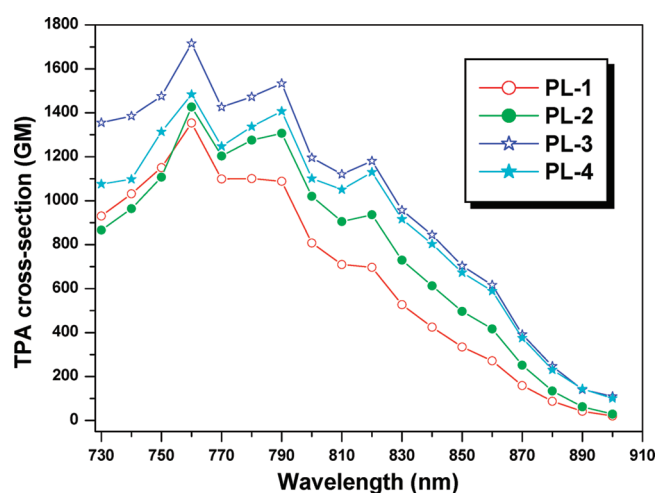


Figure 6. Two-photon absorption cross section (σ) of chromophores in THF.

bridge, benefited the ICT between the core and the two end groups, thus leading to the red-shifted ICT absorption band. Generally, the smaller the energy gap, the higher the possibility of the two-photon excitation. When σ values of the two chromophores with the same core and different N-substituted pyrroles are compared, for PL-1 and PL-2, the σ value of PL-1 was about 300 GM larger than that of PL-2, while PL-3 and PL-4 followed the same trend. This might be due to the presence of triphenylamine groups, which were linked to the pyrrole moieties together with phenyl ones through the C—N single bond, leading to possible multiple pathways for intramolecular electronic and photonic transfer. Thus, it would be a new way to increase the σ value of the chromophores by changing the aromatic rings linked to pyrrole moieties through the C—N single bond to tune the molecular size and the effective transfer.

CONCLUSIONS

A series of novel *N*-arylpyrrole-based chromophores were obtained that exhibited interesting opto-electronic behaviors. With the modification of their structures by varying the arylenevinylene units, such as fluorenylene and phenylene units, and the groups linked to pyrrole through the C—N single bond, their electronic and optical properties could be adjusted by the arylenevinylene units, indicating that the effective ICT process occurs mostly through the C=C double bond, and the N-substituted groups could give an auxiliary effect. The large σ values measured by a femtosecond laser indicated that *N*-arylpyrrole were efficient conjugated bridges, and the triphenylamine group together with phenyl linked to pyrrole might gave multiple pathways for intramolecular electronic and photonic transfer, resulting in the enhanced 2PA cross section.

ASSOCIATED CONTENT

S Supporting Information. Four figures, showing MALDI-TOF spectra of PL-1–4 This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*Phone 86-27-68755363; fax 86-27-68756757; e-mail lizhen@whu.edu.cn.

ACKNOWLEDGMENT

We are grateful to the National Science Foundation of China (21002075 and 21034006), the National Fundamental Key Research Program (2011CB932702), and the program NCET (NCET-08-0411) for financial support.

REFERENCES

- (1) (a) Rumi, M.; Ehrlich, J. E.; Heikal, A. A.; Perry, J. W.; Barlow, S.; Hu, Z.; McCord-Maughon, D.; Parker, T. C.; Röckel, H.; Thayumavan, S.; Marder, S. R.; Beljonne, D.; Brédas, J.-L. *J. Am. Chem. Soc.* **2000**, *122*, 9500. (b) Corredor, C. C.; Huang, Z. L.; Belfield, K. D. *Adv. Mater.* **2006**, *18*, 2910. (c) Raymond, J. E.; Bhaskar, A.; Goodson, T., III; Makiuchi, N.; Ogawa, K.; Kobuke, Y. *J. Am. Chem. Soc.* **2008**, *130*, 17212. (d) Williams-Harry, M.; Bhaskar, A.; Ramakrishna, G.; Goodson, T., III; Imamura, M.; Mawatari, A.; Nakao, K.; Enozawa, H.; Nishinaga, T.; Iyoda, M. *J. Am. Chem. Soc.* **2008**, *130*, 3252. (e) Bhaskar, A.; Guda, R.; Haley, M. M.; Goodson, T., III. *J. Am. Chem. Soc.* **2006**, *128*, 13972.
- (2) (a) Denk, W.; Stricker, J. H.; Webb, W. W. *Science* **1990**, *248*, 73. (b) LaFratta, C. N.; Fourkas, J. T.; Baldacchini, T.; Farrer, R. A. *Angew. Chem., Int. Ed.* **2007**, *46*, 6238. (c) Liu, B.; Zhang, H. L.; Liu, J.; Zhao, Y. D.; Luo, Q. M.; Huang, Z. L. *J. Mater. Chem.* **2007**, *17*, 2921. (d) Scott, T. F.; Kowalski, B. A.; Sullivan, A. C.; Bowman, C. N.; McLeod, R. R. *Science* **2009**, *324*, 913. (e) Guzman, A. R.; Harpham, M. R.; Süzer, Ö.; Haley, M. M.; Goodson, T. G., III. *J. Am. Chem. Soc.* **2010**, *132*, 7840.
- (3) (a) Cumpston, B. H.; Ananthaval, S. P.; Barlow, S.; Dyer, D. L.; Ehrlich, J. E.; Erskine, L. L.; Heikal, A. A.; Kuebler, S. M.; Lee, I.-Y. S.; McCord-Maughon, D.; Qin, J.; Röckel, H.; Rumi, M.; Wu, X.-L.; Marder, S. R.; Perry, J. W. *Nature* **1999**, *398*, 51. (b) Zhou, W. H.; Kuebler, S. M.; Braun, K. L.; Yu, T.; Cammack, J. K.; Ober, C. K.; Perry, J. W.; Marder, S. R. *Science* **2002**, *296*, 1106. (c) Chen, Y. S.; Tal, A.; Torrance, D. B.; Kuebler, S. M. *Adv. Funct. Mater.* **2006**, *16*, 1739. (d) Lee, K.-S.; Kim, R. H.; Yang, D.-Y.; Park, S. H. *Prog. Polym. Sci.* **2008**, *33*, 631.
- (4) (a) Reinhardt, B. A.; Brott, L. L.; Clarson, S. J.; Dillard, A. G.; Bhatt, J. C.; Kannan, R.; Yan, L.; He, G. H.; Prasad, P. N. *Chem. Mater.* **1998**, *10*, 1863. (b) Albota, M.; Beljonne, D.; Brédas, J. L.; Ehrlich, J. E.; Fu, J. Y.; Heikal, A. A.; Hess, S. E.; Kogej, T.; Levin, M. D.; Marder, S. R.; McCord-Maughon, D.; Perry, J. W.; Rockel, H.; Rumi, M.; Subramanian, G.; Webb, W. W.; Wu, X. L.; Xu, C. *Science* **1998**, *281*, 1653. (c) Belfield, K. D.; Schafer, K. J.; Mourad, W.; Reinhardt, B. A. *J. Org. Chem.* **2000**, *65*, 4475. (d) Rumi, M.; Ehrlich, J. E.; Heikal, A. A.; Perry, J. W.; Barlow, S.; Hu, Z.; McCord-Maughon, D.; Parker, T. C.; Röckel, H.; Thayumavan, S.; Marder, S. R.; Beljonne, D.; Brédas, J. L. *J. Am. Chem. Soc.* **2000**, *122*, 9500. (e) Kannan, R.; He, G. S.; Yuan, L.; Xu, F.; Prasad, P. N. *Chem. Mater.* **2001**, *13*, 1896. (f) Mongin, O.; Porrès, L.; Moreaux, L.; Mertz, J.; Blanchard-Desce, M. *Org. Lett.* **2002**, *4*, 719. (g) Mongin, O.; Porrès, L.; Charlot, M.; Katan, C.; Blanchard-Desce, M. *Chem.—Eur. J.* **2007**, *13*, 1481.
- (5) (a) Belfield, K. D.; Schafer, K. J.; Mourad, W.; Reinhardt, B. A. *J. Org. Chem.* **2000**, *65*, 4475. (b) Kim, O. K.; Lee, K. S.; Woo, H. Y.; Kim, K. S.; He, G. S.; Swiatkiewicz, J.; Prasad, P. N. *Chem. Mater.* **2000**, *12*, 684.
- (6) (a) Porres, L.; Mongin, O.; Katan, C.; Charlot, M.; Pons, T.; Mertz, J.; Blanchard-Desce, M. *Org. Lett.* **2004**, *6*, 47. (b) Lee, W. H.; Lee, H.; Kim, J. A.; Choi, J. H.; Cho, M.; Jeon, S. J.; Cho, B. R. *J. Am. Chem. Soc.* **2001**, *123*, 10658. (c) He, G. S.; Swiatkiewicz, J.; Jiang, Y.; Prasad, P. N.; Reinhardt, B. A.; Tan, L. S.; Kannan, R. *J. Phys. Chem. A* **2000**, *104*, 4805.
- (7) (a) Katan, C.; Terenziani, F.; Mongin, O.; Werts, M. H. V.; Porres, L.; Pons, T.; Mertz, J.; Tretiak, S.; Blanchard-Desce, M. *J. Phys. Chem. A* **2005**, *109*, 3024. (b) Drobizhev, M.; Karotki, A.; Dzenis, Y.; Rebane, A.; Suo, Z.; Spangler, C. W. *J. Phys. Chem. B* **2003**, *107*, 7540.
- (8) (a) Shao, P.; Huang, B.; Chen, L. Q.; Liu, Z. J.; Qin, J. G.; Gong, H. M.; Ding, S.; Wang, Q. Q. *J. Mater. Chem.* **2005**, *15*, 4502. (b) Abbotto, A.; Beverina, L.; Bozio, R.; Facchetti, A.; Ferrante, C.; Pagani, G. A.; Pedron, D.; Signorini, R. *Org. Lett.* **2002**, *4*, 1495.
- (9) (a) Zheng, S. J.; Beverina, L.; Barlow, S.; Zojer, E.; Fu, J.; Padilha, L. A.; Fink, C.; Kwon, O.; Yi, Y. P.; Shuai, Z. G.; Van Stryland, E. W.; Hagan, D. J.; Brédas, J. L.; Marder, S. R. *Chem. Commun.* **2007**, 1372. (b) Zou, L.; Liu, Z. J.; Yan, X. B.; Liu, Y.; Fu, Y.; Liu, J.; Huang, Z. L.; Chen, X. G.; Qin, J. G. *Eur. J. Org. Chem.* **2009**, 5587.
- (10) (a) Chung, S. J.; Lin, T. C.; Kim, K. S.; He, G. S.; Swiatkiewicz, J.; Prasad, P. N.; Baker, G. A.; Bright, F. V. *Chem. Mater.* **2001**, *13*, 4071. (b) Liu, Z. Q.; Fang, Q.; Cao, D. X.; Wang, D.; Xu, G. B. *Org. Lett.* **2004**, *6*, 2933.
- (11) (a) Beverina, L.; Fu, J.; Leclercq, A.; Zojer, E.; Pacher, P.; Barlow, S.; Stryland, E. W. V.; Hagan, D. J.; Brédas, J. L.; Marder, S. R. *J. Am. Chem. Soc.* **2005**, *127*, 7282. (b) Chung, S. J.; Zheng, S.; Odani, T.; Beverina, L.; Fu, J.; Padilha, L. A.; Biesso, A.; Hales, J. M.; Zhan, X.; Schmidt, K.; Ye, A. J.; Zojer, E.; Barlow, S.; Hagan, D. J.; Stryland, E. W.; Yi, V. Y. P.; Shuai, Z. G.; Pagani, G. A.; Brédas, J. L.; Perry, J. W.; Marder, S. R. *J. Am. Chem. Soc.* **2006**, *128*, 14444. (c) Zheng, S.; Leclercq, A.; Fu, J.; Beverina, L.; Padilha, L. A.; Zojer, E.; Schmidt, K.; Barlow, S.; Luo, J.; Jiang, S.; Jen, A. K. Y.; Yi, Y.; Shuai, Z. G.; Stryland, E. W. V.; Hagan, D. J.; Brédas, J. L.; Marder, S. R. *Chem. Mater.* **2007**, *19*, 432.
- (12) (a) Li, Q.; Lu, L.; Zhong, C.; Huang, J.; Huang, Q.; Shi, J.; Jin, X.; Peng, T.; Qin, J.; Li, Z. *Chem.—Eur. J.* **2009**, *15*, 9664. (b) Li, Q.; Lu, L.; Zhong, C.; Shi, J.; Huang, Q.; Jin, X.; Peng, T.; Qin, J.; Li, Z. *J. Phys. Chem. B* **2009**, *113*, 14588. (c) Li, Q.; Lu, C.; Zhu, J.; Fu, E.; Zhong, C.; Li, S.; Cui, Y.; Qin, J.; Li, Z. *J. Phys. Chem. B* **2008**, *112*, 4545. (d) Li, Q.; Zou, J.; Chen, J.; Liu, Z.; Qin, J.; Li, Z.; Cao, Y. *J. Phys. Chem. B* **2009**, *113*, 5816.
- (13) Isabella, B.; Sabine, H.; Herbert, M. *Eur. J. Org. Chem.* **2002**, 3162.
- (14) Wen, S. P.; Pei, J. N.; Zhou, Y. H.; Li, P. F.; Xue, L. L.; Li, Y. W.; Xu, B.; Tian, W. J. *Macromolecules* **2009**, *42*, 4977.
- (15) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, H.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, revision E.1*; Gaussian, Inc., Pittsburgh, PA, 2003.