Phenothiazine−Anthraquinone Donor−Acceptor Molecules: Synthesis, Electronic Properties and DFT-TDDFT Computational Study

Wen-Wei Zhang,* Wei-Li Mao,† Yun-Xia Hu,† Zi-Qi Tian,† Zhi-Lin Wang,† and Qing-Jin Meng*

State Key Laboratory of Coordination Chemistry, Nanjing National Laboratory of Microstructures, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, 210093 P.R. China

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Two donor−acceptor molecules with different π-electron conjugative units, 1-((10-methyl-10*H*-phenothiazin-3-yl)ethynyl)anthracene-9,10-dione (AqMp) and 1,1′-(10-methyl-10*H*-phenothiazine-3,7-diyl)bis(ethyne-2,1-diyl)dianthracene-9,10-dione (Aq_2Mp), have been synthesized and investigated for their photochemical and electrochemical properties. Density functional theory (DFT) calculations provide insights into their molecular geometry, electronic structures, and properties. These studies satisfactorily explain the electrochemistry of the two compounds and indicate that larger conjugative effect leads to smaller HOMO−LUMO gap (E_g) in Aq_2Mp. Both compounds show ICT and $\pi \rightarrow \pi^*$ transitions in the UV−visible range in solution, and Aq_2Mp has a bathochromic shift and shows higher oscillator strength of the absorption, which has been verified by time-dependent DFT (TDDFT) calculations. The differences between AqMp and Aq_2Mp indicate that the structural and conjugative effects have great influence on the electronic properties of the molecules.

Introduction

Donor−acceptor (D−A) molecules have recently attracted considerable academic and technological research attention since they are finding growing applications in molecular electronics and optoelectronics, including organic light-emitting diodes (OLEDs),[1,2] electrogenerated chemiluminescence (ECL),[3,4] photovoltaic devices,[5] biochemical fluorescent technology,[6] and nonlinear optics.[7] Usually, designing proper D or A building blocks over a wide range of different functional units could rationally control unique electrical, optical, redox, and electroluminescent properties of the D−A materials. Moreover, their physical properties could also be adjusted by appropriate manipulation of their chemical structures such as different connections linking the D/A building blocks, distance between the D/A units, and molecular geometry in the D−A systems. So synthesis and investigation of new D−A molecules are essential for improving the electronic and optoelectronic properties of such materials.

Among the current explored D−A molecules, triarylamine,[5c,8] carbazole,[5c,9] fluorene,[10] thiophene, and oligothiophenes[11] have mostly been used as electron-donating moieties, whereas oxadiazole,[12] diarylboron,[13] quinoline,[3e,4d,5c,9a,c,14] quinoxaline,[15] thienopyrazine,[16] and benzothiadiazole[8e,17] are commonly used as electron-accepting moieties. Recently, phenothiazine and its derivatives, the outstanding heterocyclic compounds with high electron-donor ability, are getting more research interest because of their favorable electro-optical properties, which can make these molecules good candidates as light-emitting diodes,[18] organic field effect transistors,[19] and photovoltaic cells.[20] Besides their potential applications in materials science, phenothiazines are also active in pharmacology as effective pharmacophores in tranquilizers, antituberculosis agents, antitumor agents, and bactericides,[21] and they may even be helpful in treating with the new variant Creutzfeldt−Jacob disease (nvCJD)[22] and HIV-1.[23] On the other hand, it is well-known that quinones are widely distributed in nature and function as pigments and intermediates in cellular respiration and photosynthesis, so they are often employed as electron and hydrogen atom acceptors in thermal and photochemical processes in artificial systems.[24] Nowadays, current investigations also show that some quinones, especially 9,10-anthraquinones, are responsible for DNA damage and possess anticancer activities.[25]

Up to now, although a considerable amount of work has been published on the D−A compounds concerning phenothiazines or anthraquinones on account of their excellent electroactive and photoactive properties, fewer studies were emphasized on D−A chromophores involving both phenothiazines and anthraquinones. This motivates us to design novel D−A architectures using phenothiazines as donors and anthraquinones as acceptors to probe the electronic structure/property relationships.

In this general context, we present herein the synthesis and electrical properties of two new D−A compounds, 1-((10-methyl-10*H*-phenothiazin-3-yl)ethynyl)anthracene-9,10-dione (AqMp) and 1,1′-(10-methyl-10*H*-phenothiazine-3,7-diyl)bis-(ethyne-2,1-diyl)dianthracene-9,10-dione(Aq_2Mp), in which the donor 10-methyl-10*H*-phenothiazine (Mp) and the acceptor 9,10-anthraquinone (Aq) are covalently linked by ethynylene spacers (Scheme 1). It is evident that the AqMp dyad and Aq_2Mp triad have different π-electron conjugative units, which may lead to different electronic structure and different interchromophoric electronic interactions. Detailed results and discussion are elaborated in the following sections.

Experimental Section

Materials. All chemicals were purchased reagent grade and used without further purification. Dry dichloromethane was obtained by refluxing and distilling over CaH_2 under nitrogen. Anhydrous triethylamine was dried over KOH overnight, and

* Corresponding authors. Tel.: +86-25-83595830. Fax: +86-25-83595830. E-mail: W.-W.Z., wwzhang@nju.edu.cn; Q.-J.M., mengqj@nju.edu.cn.

† E-mail: W.-L.M, maoweili_04@sina.com; Y.-X.H., yunxiahu1214@163.com; Z.-Q.T., tzqzwd@163.com; Z.-L.W., wangzl@nju.edu.cn.

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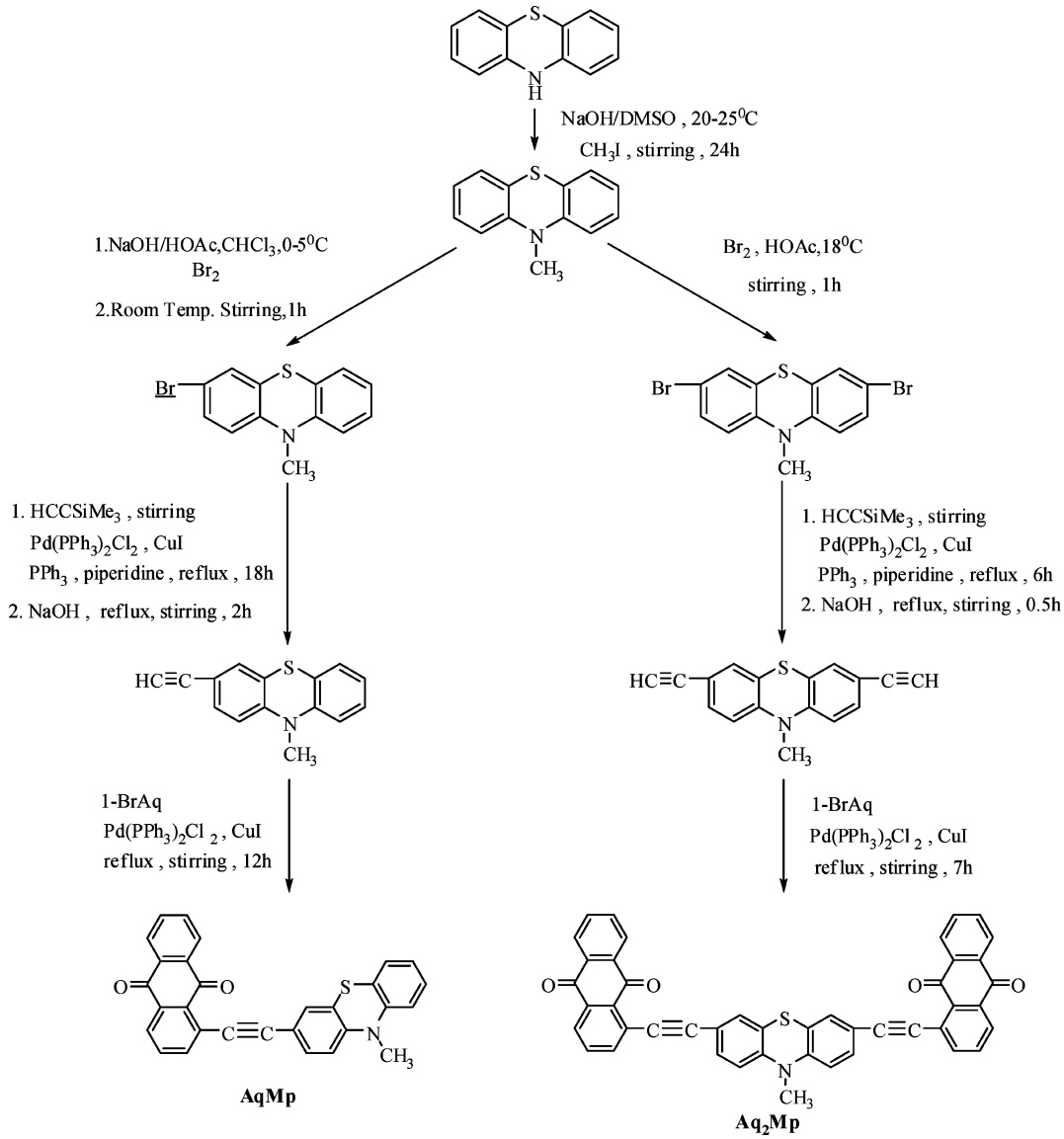
SCHEME 1: Synthetic Procedure of the Two D−A Compounds AqMp and Aq_2Mp



then distilled from fresh KOH under nitrogen. 10-Methyl-10*H*-phenothiazine,[26] 3-bromo-10-methyl-10*H*-phenothiazine,[27] 3,7-dibromo-10-methyl-10*H*-phenothiazine,[27] 3-ethynyl-10-methyl-10*H*-phenothiazine,[28] 3,7-diethynyl-10-methyl-10*H*-phenothiazine,[28] and 1-bromo-9,10-anthraquinone[29] were prepared according to literature procedures. All the reactions were monitored by TLC (silica gel plates, GF254). Silica gel 60 (100−200 mesh) was used for column chromatography.

Instruments and Measurements. Elemental analyses (C, H, and N) were carried out on a Perkin-Elmer 240 analyzer. The IR spectra were obtained on a VECTOR TM 22 spectrometer with KBr pellets in the 4000−400 cm^{-1} region. The electronic absorption spectra were carried out on a LAMBDA-35 UV/vis spectrophotometer. ^1H NMR spectra were recorded on a Bruker DRX-500 spectrometer at ambient temperature with tetramethylsilane as an internal reference. The MALDI-TOF-MS spectra were measured on a Bruker Daltonics flexAnalysis autoflexTOF/TOF spectrometer using cinnamic acid as a matrix. Cyclic voltammetry experiments were performed under nitrogen in dry and degassed CH_2Cl_2 at a scan rate of 100 mV s^{-1} with a CHI 660B potentiostatic instrument at room temperature. The three-electrode cell comprises a 1 mm platinum disk working electrode, a platinum wire auxiliary electrode, and an Ag/Ag^+ reference electrode. The electrolyte is *n*-Bu_4NClO_4 (0.1 mol dm^{-3}). The potentials were corrected to the internal standard of Fc/Fc^+ in CH_2Cl_2 (126 mV vs Ag/Ag^+ electrode).

Theoretical Methods. All calculations on compounds AqMp and Aq_2Mp, together with their building units of 9,10-anthraquinone (Aq) and 10-methyl-10*H*-phenothiazine (Mp), were done on the Gaussian03 program package[30] by using density functional theory (DFT) and time-dependent DFT (TDDFT): Becke's three-parameter functional[31] combined with Lee, Yang, and Parr's correlation functional[32] (B3LYP), along with 6-31G* basis set, was used. Geometry optimizations attempt to locate the minima on the potential energy surface to predict equilibrium structures of a given molecule. Single-point energy calculations of the electronic properties of AqMp and Aq_2Mp at their optimized ground-state geometries were carried out by utilizing DFT at the B3LYP/6-31G* level. All the geometries and electronic properties were calculated by assuming AqMp and Aq_2Mp to be isolated molecules. The lowest 20 singlet−singlet transitions up to a wavelength of ca. 260 nm for AqMp and 30 singlet−singlet transitions for Aq_2Mp up to a wavelength of ca. 310 nm were computed by TDDFT calculations.

Synthesis of AqMp. In N_2 atmosphere, 3-ethynyl-10-methyl-10*H*-phenothiazine (67.0 mg, 0.2823 mmol), 1-bromo-9,10-

anthraquinone (87.1 mg, 0.3034 mmol), bis(triphenylphosphine)-palladium(II) dichloride (2.2 mg, 0.003103 mmol), and copper(I) iodide (1.2 mg, 0.006301 mmol) were dispersed in anhydrous triethylamine (10 mL) and the suspension was refluxed with stirring for 12 h until complete consumption of 3-ethynyl-10-methyl-10*H*-phenothiazine (monitored by TLC). Then the solvent was evaporated under vacuum. The residue was dissolved in dichloromethane and washed with water for several times, dried with anhydrous $MgSO_4$ and filtered off. The product in the filtrate was chromatographed on silica gel using ether−hexane (1:8 v/v) as eluent. The third red-brown band was collected, and then evaporated under vacuum to give red-brown solid. Yield: 35.5 mg (27.5%). IR (KBr disk): 2197 cm^{-1} ($\nu_{C\equiv C}$), 1673 cm^{-1} ($\nu_{C=O}$). ^1H NMR (500 MHz, $CDCl_3$): δ 8.35 (d, J = 7.5 Hz, 1H), 8.28 (t, J = 7.5 Hz, 1H), 7.92 (d, J = 7.5 Hz, 1H), 7.82−7.75 (m, 2H), 7.71 (t, J = 7.5 Hz, 1H), 7.52 (d, J = 8.0 Hz, 1H), 7.48 (s, 1H), 7.17 (t, J = 7.5 Hz, 1H), 7.14 (d, J = 7.5 Hz, 1H), 6.95 (t, J = 7.5 Hz, 1H), 6.82 (d, J = 8.0 Hz, 1H), 6.79 (d, J = 8.5 Hz, 1H), 3.40 (s, 3H). Anal. Calcd for $C_{29}H_{17}O_2NS$: C, 78.53; H, 3.86; N, 3.16. Found: C, 78.31; H, 4.04; N, 3.12. MS: m/z 444.206 $[M + 1]^+$ (calcd 444.106).

Synthesis of Aq_2Mp. In N_2 atmosphere, the reaction mixtures of 3,7-diethynyl-10-methyl-10*H*-phenothiazine (129.6 mg, 0.4959 mmol) and 1-bromo-9,10-anthraquinone (290.1 mg, 1.0104 mmol), together with bis(triphenylphosphine)palladium(II) dichloride (3.6 mg, 0.005129 mmol) and copper(I) iodide (2.0 mg, 0.01050 mmol) in anhydrous triethylamine (20 mL) were stirred and refluxed for about 7 h until complete consumption of 3,7-diethynyl-10-methyl-10*H*-phenothiazine (monitored by TLC). Then the solvent was removed under vacuum. The residue was dissolved in dichloromethane and washed with water for several times and then dried with anhydrous $MgSO_4$. After filtration and concentration, the desired product Aq_2Mp was separated by column chromatography on silica gel using dichloromethane as eluent. Yield: 170.0 mg (50.9%). IR (KBr disk): 2194 cm^{-1} ($\nu_{C\equiv C}$), 1673 cm^{-1} ($\nu_{C=O}$). ^1H NMR (500 MHz, $CDCl_3$): δ 8.38 (d, J = 7.5 Hz, 2H), 8.32 (d, J = 7.5 Hz, 2H), 8.24 (t, J = 7.5 Hz, 2H), 7.95 (d, J = 8.0 Hz, 2H), 7.83−7.79 (m, 4H), 7.74 (t, J = 7.5 Hz, 2H), 7.56 (d, J = 8.0 Hz, 2H), 7.51 (s, 2H), 6.84 (d, J = 8.0 Hz, 2H), 3.45 (s, 3H). Anal. Calcd for $C_{45}H_{23}O_4NS$: C, 80.22; H, 3.44; N, 2.08. Found: 80.27; H, 3.59; N, 1.95. MS: m/z 674.098 $[M + 1]^+$ (calcd 674.142).

Results and Discussion

Synthesis and Characterization of Materials. Scheme 1 describes the synthetic procedures and the structures of the main intermediates and the respective products. The target dyad and triad compounds, comprising phenothiazine as electron-donor and anthraquinone as acceptor chromophore linked by the π-conjugated spacer of ethynylene, were successfully synthesized by the Sonogashira cross-coupling reaction using bis-(triphenylphosphine)palladium(II) and copper(I) iodide as catalysts and triethylamine as a base. They were fully characterized by IR, ^1H NMR spectra, MS, and element analysis. Both compounds exhibited the characteristic −C≡C− triple bond and the C=O carbonyl stretching vibrations around 2200 and 1670 cm^{-1}, respectively. They also showed the characteristic resonance bands of the anthraquinonyl moiety in the 8.35−7.55 ppm range and the characteristic resonance bands of the phenothiazinyl moiety in the 7.52−6.79 ppm range and at about 3.4 ppm. In addition, MALDI-TOF-MS experiments revealed the most prominent peak at m/z 444.206 and 675.087, respectively, which were perfectly in agreement with the corresponding calculated value of $[M + 1]^+$, and displayed an isotopic pattern identical with the simulated one. All the results given above were in good accordance with the proposed structures.

TABLE 1: UV−Vis Absorption Properties of AqMp and Aq_2Mp in Solvents of Varying Polarity

compd	solvent	λ_{max}^{abs} (nm)	ε (10^4 M^{-1} cm^{-1})	λ_{edge} (nm)[a]	E_g^{opt} (eV)[b]
AqMp	toluene	283	4.61		
		370	1.88		
		474	0.72	570	2.18
	CH_2Cl_2	258	4.67		
		274	4.67		
		369	1.22		
		473	0.44	560	2.21
	THF	254	9.60		
		365	2.50		
		470	0.92	556	2.23
Aq_2Mp	toluene	284	4.62		
		372	2.11		
		480	1.30	578	2.15
	CH_2Cl_2	259	6.14		
		276	5.78		
		371	1.68		
		477	0.89	565	2.20
	THF	256	9.85		
		369	2.64		
		472	1.53	559	2.22

[a] The onset value of absorption spectrum in long wavelength direction. [b] The optical band gap was obtained from the equation $E_g^{opt} = 1240/\lambda_{edge}$.

Electronic Properties. AqMp and Aq_2Mp could dissolve in some normal organic solvents, such as chloroform, toluene, THF, etc. Their solution-phase UV−vis absorption spectra in different polarity solvents were recorded at room temperature. All the photoelectrical properties are collected in Table 1. Representative optical absorption spectra of the two D−A molecules in dilute dichloromethane are shown in Figure 1. Both of them display several characteristic bands in different solvents: two bands in the 470−480 and 365−375 nm ranges with lower intensity; one or two bands in the 250−290 nm range with higher intensity. Weak solvatochromism is observed in the absorption bands for both compounds. Generally, these bands can be assigned to ICT (intramolecular charge transfer) and $\pi \rightarrow \pi^*$ and n−π^* transitions.[3b,e,24c,28,33,34b] The computational study discussed later will give a detailed band assignment.

The main difference in the absorption spectra of these two compounds is that all the ICT, $\pi \rightarrow \pi^*$, and n−π^* transitions of Aq_2Mp are bathochromic shifts compared with those of AqMp. Moreover, the oscillator strength (ε_{max}) of all the bands of Aq_2Mp is larger than that of AqMp, suggesting a higher probability for ICT, $\pi \rightarrow \pi^*$, and n−π^* transitions in Aq_2Mp.[34] All the above indicates a better electronic coupling between the Mp and Aq subunits and a larger π-conjugative effect in Aq_2Mp. Actually, it can be understandable that better coplanarity between Mp and Aq moieties (vide post) and more conjugative subunits in Aq_2Mp will lead to a more remarkable π-electron delocalization and a larger π-conjugation.

Electrochemical Properties. The electrochemical properties of compounds AqMp and Aq_2Mp were measured by cyclic voltammograms (CV). Both of them are electrochemically stable. Figure 2 shows their CV in dichloromethane. Three couples of reversible or quasi-reversible redox peaks were observed for each molecule under CV conditions. The reversible one-electron oxidation process around 0.5 V vs Fc/Fc^+ is derived from the phenothiazinyl moiety, resulting in the formation of phenothiazinyl radical cation.[3b,e,34b] The other two quasi-

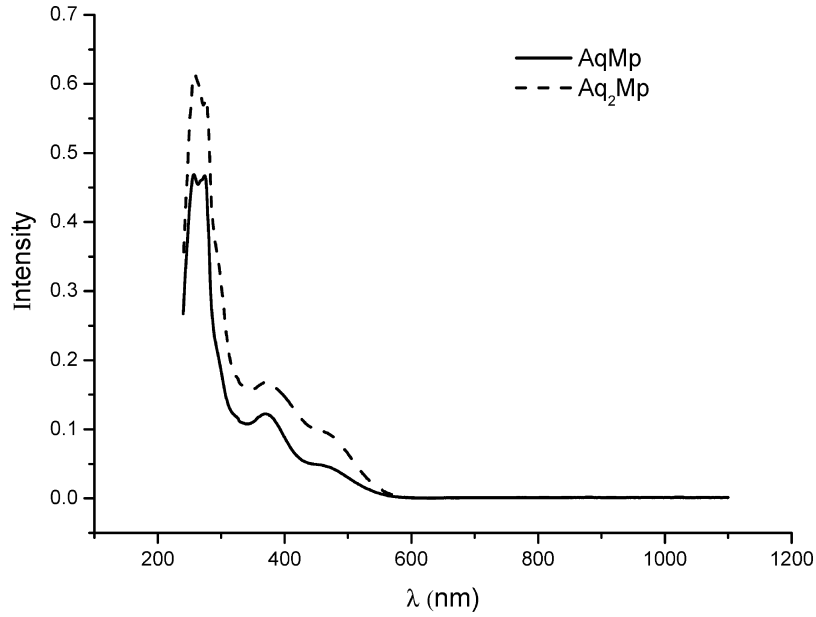


Figure 1. UV−vis absorption spectra of AqMp (1.0×10^{-5} mol·L^{-1}) and Aq_2Mp (1.0×10^{-5} mol·L^{-1}) in dichloromethane.

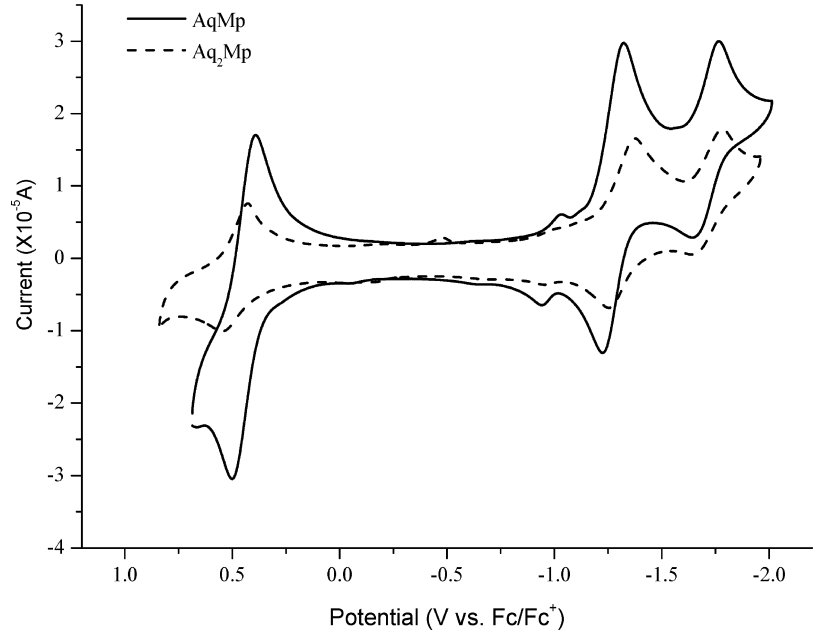


Figure 2. Cyclic voltammograms of compounds AqMp and Aq_2Mp in dichloromethane (20 °C, 1 mM of AqMp and 0.5 mM of Aq_2Mp, 0.1 M TBAP, Pt disc as a working electrode, Ag/Ag^+ as a reference electrode, and Pt wire as a counter electrode, scan rate 100 mV/s).

TABLE 2: Electrochemical Potentials of Compounds AqMp and Aq_2Mp (vs Fc^+/Fc)

compd	redox couple	E_{pc} (V)	E_{pa} (V)	$E_{1/2}$ (V)
AqMp	$Mp^{\bullet+}/Mp$	0.390	0.501	0.446
	Aq/Aq^-	−1.323	−1.226	−1.275
	Aq^-/Aq^{2-}	−1.766	−1.640	−1.703
Aq_2Mp	$Mp^{\bullet+}/Mp$	0.427	0.546	0.486
	Aq/Aq^-	−1.371	−1.255	−1.313
	Aq^-/Aq^-	−1.782	−1.641	−1.712

reversible one-electron reduction processes at about −1.3 and −1.7 V vs Fc/Fc^+ are originated from the anthraquinonyl unit, leading to the formation of anthraquinonyl mono- and dianions.[35] The data of the redox peaks and the corresponding half-wave potentials are detailed in Table 2. The close match of the redox potentials of both AqMp and Aq_2Mp to those of the parent D/A building blocks, Mp and Aq, suggests selective oxidation of Mp and reduction of Aq subunits in each D−A molecule. It implies that the orbital of the HOMO in the D−A molecules is almost localized on the phenothiazinyl moiety, while that of LUMO is nearly localized on the anthraquinonyl moiety, and hence weak intramolecular D/A coupling exists in the ground state.[3e,36] This will also be supported by DFT calculations on them where the orbital coefficient in HOMO is predominantly phenothiazinyl centered, while in the LUMO it is almost anthraquinonyl centered (vide post).

In comparison with the electrochemical potentials of AqMp and Aq_2Mp, it is clearly seen that the oxidation process of Aq_2Mp is anodic shift to higher potential, while its reduction process is cathodic shift to lower potential than that of AqMp. It is in accordance with the results of some other mono- and diacceptor substituted phenothiazines.[37] This can be attributed not only to stereoelectronic aspect but also to π-conjugative

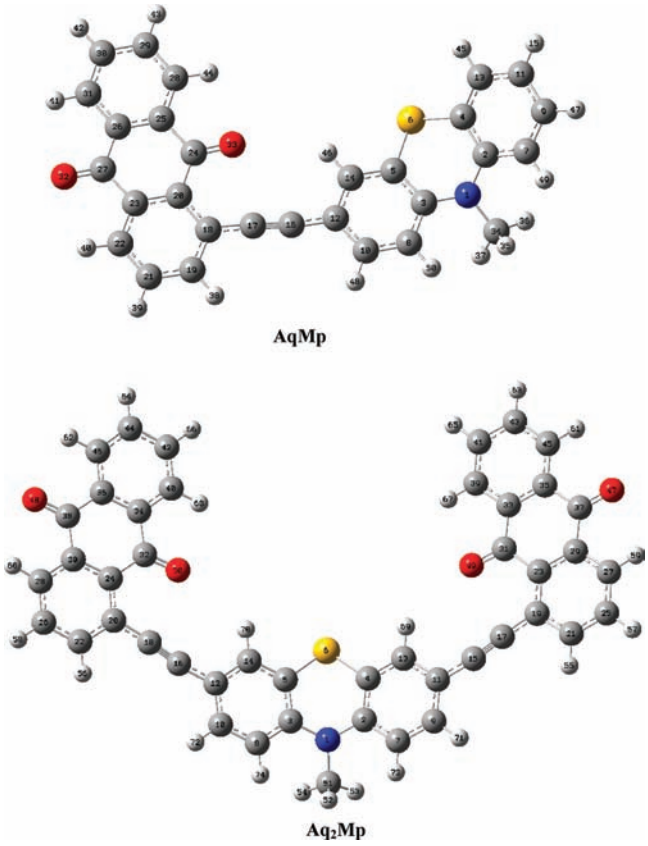


Figure 3. Optimized ground-state geometries of AqMp and Aq_2Mp as predicted by quantum-chemical calculations.

effect. On the one hand, better coplanarity is found in Aq_2Mp than in AqMp (vide post), which favors the π-orbital overlap and the orbital mixing. On the other hand, it is evident that Aq_2Mp is composed of more π-conjugative subunits, which results in larger π-conjugative effect between the two anthraquinonyl moieties and one phenothiazinyl moiety. Thus the stability of Aq_2Mp is better than that of AqMp. From the quantum-chemical calculation detailed below, the same result can also be obtained since Aq_2Mp has lower HOMO and LUMO energy. As a consequence, it is more difficult for Aq_2Mp to lose or get electrons. That is to say, for compound Aq_2Mp, the oxidative phenothiazinyl radical cation is easier to get electron to change back to its reduction state Mp, and the reductive anthraquinonyl anion is also easier to lose electrons to turn back to its oxidation state Aq. Therefore, more positive potential corresponding to the phenothiazinyl centered oxidation and more negative potential corresponding to the anthraquinonyl centered reduction of Aq_2Mp will be obtained. The experimental results match the theoretical analysis very well.

Study on Quantum-Chemical Calculation. In an effort to understand the optical and electronic properties of these two conjugated compounds at the molecular level, density functional theory (DFT) was used to calculate the electronic structures and time-dependent DFT (TDDFT) was adopted to investigate the ground to excited-state transitions. Figure 3 shows the optimized ground-state geometries of both AqMp and Aq_2Mp obtained with the B3LYP/6-31G* basis set. Some main bond lengths, bond angles, and dihedral angles of AqMp and Aq_2Mp as predicted by quantum-chemical calculations are shown in Tables 3 and 4, respectively. In both conjugated D−A compounds, the −C≡C− triple bond length is 122.1 pm, a little longer than that in unconjugated molecules. The C−C single bond length next to the ethynylene bond is about 142.0 pm, a little shorter

TABLE 3: Selected Bond Lengths (pm), Bond Angles (deg), and Dihedral Angles (deg) of AqMp As Predicted by Quantum-Chemical Calculations

bond lengths		bond and dihedral angles	
C16−C17	122.1	C12−C16−C17	172.7
C12−C16	142.0	C16−C17−C18	176.0
C17−C18	141.9	C2−N1−C3−C5	35.7
C24−O33	125.4	C2−C4−S6−C5	34.0
C27−O32	125.4	C3−N1−C2−C4	−36.5
		C3−C5−S6−C4	−34.7

TABLE 4: Selected Bond Lengths (pm), Bond Angles (deg), and Dihedral Angles (deg) of Aq_2Mp As Predicted by Quantum-Chemical Calculations

bond lengths		bond and dihedral angles	
C15−C17	122.1	C11−C15−C17	172.6
C11−C15	142.0	C15−C17−C19	176.1
C17−C19	141.9	C12−C16−C18	172.6
C16−C18	122.1	C16−C18−C20	176.1
C12−C16	142.0	C2−N1−C3−C5	35.0
C18−C20	141.9	C2−C4−S6−C5	34.2
C31−O49	125.4	C3−N1−C2−C4	−35.0
C37−O47	125.4	C3−C5−S6−C4	−34.2
C32−O50	125.4		
C38−O48	125.4		

than the common C−C single bond length. The C═O carbonyl bond length in them is 125.4 pm, a little longer than that in the parent compound of Aq (122.8 pm) calculated by the same method. In addition, the −C≡C− bond angle almost displays linearity (for AqMp: C12−C16−C17, 172.7°; C16−C17−C18, 176.0°. For Aq_2Mp: C11−C15−C17 and C12−C16−C18, 172.6°; C15−C17−C19 and C16−C18−C20, 176.1°). So it is obvious that the π electrons in the two D−A molecules are delocalized from the data given above. Since the coplanarity of the Aq subunit and the benzo ring of the Mp subunit are fairly well from the DFT results, and the ethynylene linker is almost coplanar with both the Aq moiety and the benzo ring of the Mp moiety, the dihedral angle of the heterocycle in the characteristic butterfly conformation of the Mp core unit will dominantly determine the extent of coplanarity and electronic coupling between the D/A subunits. For compound AqMp, the dihedral angles of C2−N1−C3−C5, C2−C4−S6−C5, C3−N1−C2−C4, and C3−C5−S6−C4 in the Mp moiety are +35.7°, +34.0°, −36.5°, and −34.7°, respectively. For Aq_2Mp, the dihedral angles of them are +35.0°, +34.2°, −35.0°, and −34.2°, respectively. So it can be seen from the data that the coplanarity of the phenothiazinyl moiety in compound Aq_2Mp is a little better than that in AqMp. This would enable better electronic coupling between Mp and Aq units and result in superior conjugated effect in the ground state of Aq_2Mp, which satisfactorily explains the experimental photo- and electrochemical properties detailed above.

Figure 4 shows the plots of the most representative molecular frontier orbitals in the ground states of AqMp and Aq_2Mp. Other frontier orbitals relevant to discussion are available as Supporting Information. In both molecules, the HOMOs are nearly completely localized between the Mp moiety and the ethynylene bridge, while the LUMOs, (LUMO+1)s and (LUMO+2)s are almost predominantly localized between the Aq moiety and the ethynylene bridge. This indicates that the HOMO → LUMO, HOMO → LUMO+1, and HOMO → LUMO+2 absorption transitions bear a significant intramolecular charge-transfer (ICT) character. The other absorption bands dominantly transferred between the Mp or Aq characteristic orbitals suggest that these kinds of transitions are mainly of $\pi \rightarrow \pi^*$ character. The most

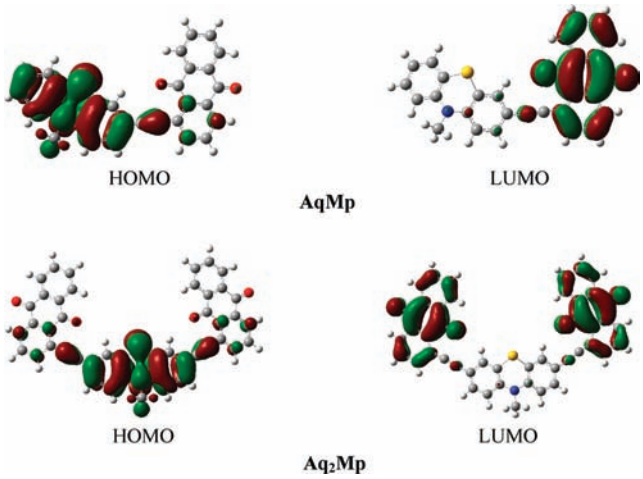


Figure 4. HOMO and LUMO orbitals in the optimized ground-state structure of AqMp and Aq_2Mp.

representative calculated optical transitions for them are collected in Table 5. Except for the calculated lowest-energy ICT band of HOMO → LUMO transition with lower oscillator strength f not being observed in the two compounds, other calculated transitions qualitatively agree with the experimental ones.

As for AqMp, the experimental band found at 473 nm corresponds to the transition calculated at 445 nm. This band is originated from HOMO → LUMO+1 transition with ICT character. Another band exhibited at 369 nm is mainly originated from two transitions, HOMO−1 → LUMO+1and HOMO−7 → LUMO, which can be assigned to ICT (58%) and $\pi \rightarrow \pi^*$ (33%) transition of Aq moiety due to the orbital characters of the corresponding starting and arriving states (see Supporting Information). At shorter wavelength, an intense band found at 274 nm together with a shoulder around 299 nm may be related to two calculated bands at 285 and 318 nm, respectively. According to the orbital characters of the corresponding starting and arriving states of the two bands (see Supporting Information), for examples, HOMO−9 and LUMO orbitals are mainly Aq localized, while HOMO and LUMO+4 orbitals are dominantly Mp localized; the absorption band at 285 nm is basically due to the $\pi \rightarrow \pi^*$ transition of the Aq moiety (81%), while the absorption band at 318 nm is mostly attributed to the $\pi \rightarrow \pi^*$ transition of the Mp moiety (60%). Moreover, the band at 285 nm also includes the $\pi \rightarrow \pi^*$ transition of the Mp moiety (HOMO → LUMO+6), and the band at 318 nm contains some ICT transitions (HOMO → LUMO+2 and HOMO−2 → LUMO+1) and a little $\pi \rightarrow \pi^*$ transition of the Mp moiety (HOMO → LUMO+5). The percentage of each composition is also clearly listed in Table 5. It is worth noting that the $\pi \rightarrow \pi^*$ transitions of AqMp arising from the Aq or Mp moiety at different wavelengths are in fairly good agreement with the results obtained by TDDFT from the parent molecules of Aq and Mp (see Supporting Information). So from the data given above, it can be deduced that the calculated absorption bands in AqMp are excellently consistent with the experimental values.

Similarly, concerning Aq_2Mp, analogous results can be obtained from TDDFT study. The experimental absorption band of 477 nm at longer wavelength is of ICT character relevant to several calculated bands from 470 to 430 nm composed of a set of mixed ICT transitions between different orbitals listed in Table 5. Among them, the calculated band at 464 nm coming from the HOMO → LUMO+2 transition with larger oscillator strength is of most importance. The band found at 371 nm is derived from several transitions with different features: 350 nm with larger oscillator strength is of ICT character, 337 nm with lower oscillator strength is of $\pi \rightarrow \pi^*$ and n → π^* character relevant to the Aq moiety, and 334 nm is mainly of ICT character. The composition and percentage of each transition are also given in Table 5. Just as that discussed in AqMp, the calculated absorption bands in Aq_2Mp are also in good agreement with the experimental results.

The calculated LUMO and HOMO energy levels of the two molecules together with their parent building blocks of Mp and Aq are listed in Table 6. The phenothiazinyl centered HOMO levels for compounds AqMp and Aq_2Mp are −5.11 and −5.14

TABLE 5: Main Calculated Optical Transitions for AqMp and Aq_2Mp

compd	cal (nm)	f	composition (%)	character	exp (nm)
AqMp	671.5	0.0850	100 (HOMO → LUMO)	ICT	
	445.2	0.3226	100 (HOMO → LUMO+1)	ICT	473
	344.9	0.2186	58 (HOMO−1 → LUMO+1)	ICT	369
			33 (HOMO−7 → LUMO)	$\pi \rightarrow \pi^*$ (Aq)	
	317.8	0.1232	60 (HOMO → LUMO+4)	$\pi \rightarrow \pi^*$ (Mp)	299
			10 (HOMO → LUMO+2)	ICT	(shoulder peak)
			8 (HOMO−2 → LUMO+1)	ICT	
			6 (HOMO → LUMO+5)	$\pi \rightarrow \pi^*$ (Mp)	
	284.8	0.2010	81 (HOMO−9 → LUMO)	$\pi \rightarrow \pi^*$ (Aq)	274
			10 (HOMO → LUMO+6)	$\pi \rightarrow \pi^*$ (Mp)	
Aq_2Mp	678.1	0.1037	100 (HOMO → LUMO)	ICT	
	470.4	0.1378	30 (HOMO−2 → LUMO)	ICT	477
			55 (HOMO−1 → LUMO+1)	ICT	
	469.0	0.1070	25 (HOMO−2 → LUMO+1)	ICT	
			70 (HOMO−1 → LUMO)	ICT	
	464.2	0.3542	90 (HOMO → LUMO+2)	ICT	
	429.8	0.1388	100 (HOMO → LUMO+3)	ICT	
	350.1	0.3696	55 (HOMO−2 → LUMO+2)	ICT	371
			12 (HOMO−1 → LUMO+3)	ICT	
			26 (HOMO → LUMO+4)	ICT	
	336.8	0.1209	48 (HOMO−8 → LUMO+1)	$\pi \rightarrow \pi^*$ (Aq)	
			39 (HOMO−7 → LUMO)	n → π^* (Aq)	
			13 (HOMO−6 → LUMO)	n → π^* (Aq)	
	333.8	0.1014	82. (HOMO−1 → LUMO+3)	ICT	
			13 (HOMO−2 → LUMO+2)	ICT	

TABLE 6: Calculated DFT Energy Levels of Frontier Orbitals (eV), E_g(HOMO−LUMO Band Gap) (eV), Ground-State Mulliken Atomic Charges and Dipole Moments (debye) of Compounds AqMp, Aq_2Mp, Mp, and Aq

				Mulliken atomic charges			
compd	LUMO	HOMO	E_g	N	S	O	dipole moment
AqMp	−2.90	−5.11	2.21	−0.7146	0.4094	−0.4152, −0.4044	3.86
Aq_2Mp	−2.95	−5.14	2.19	−0.7194	0.4236	−0.4156, −0.4042	3.93
Mp	−0.56	−5.13	4.57	−0.2473	0.1514		2.46
Aq	−3.17	−7.36	4.19			−0.4857, −0.4890	0.0031

eV, respectively, which are very close to the HOMO level of the parent Mp (−5.13 eV). The anthraquinonyl centered LUMO levels for them are −2.90 and −2.95 eV, respectively, which are very close to the LUMO level of the parent Aq (−3.17 eV). This clearly confirms the previously discussed hypothesis of site-selective oxidation occurring on the donor phenothiazinyl unit and site-selective reduction arising from the acceptor anthraquinonyl moiety in the electrochemistry. Moreover, the slightly higher HOMO and LUMO energy level in compound AqMp compared to Aq_2Mp indicates that the stability of AqMp is lower than that of Aq_2Mp. So AqMp is a little easier to lose or get electrons to occur site-selective oxidation or site-selective reduction. Therefore, the DFT calculations predict the experimentally observed trends in the redox properties of these two compounds very well.

The calculated HOMO−LUMO gaps (E_g) for conjugative π-electron extending molecules AqMp and Aq_2Mp are 2.21 and 2.19 eV, respectively, which are excellently consistent with the experimentally estimated optical band gaps (E_g^{opt}) shown in Table 1. The calculated E_g value of each π-conjugated molecule is much lower than that of the parent blocking compounds Mp and Aq, where their E_g values are 4.57 and 4.19 eV, respectively. So the HOMO−LUMO gaps of the D−A molecules could be decreased after the donor and acceptor subunits were bridged by the π-linker to emerge a larger π-conjugated system. Besides that, the E_g value of Aq_2Mp is a little lower, comparable to that of AqMp, indicating larger delocalization and conjugative effect of Aq_2Mp. This is also in agreement with the result obtained from the optimized structures by quantum chemical calculations discussed above.

In addition, it can be seen clearly from Table 6 that the Mulliken atomic charges of N, S, and O are changed a lot after the parent blocking units of Mp and Aq are combined to form the two D−A compounds of AqMp and Aq_2Mp. The negative charges of O atoms in the conjugated D−A molecules are lower than those in Aq, which indicates that the charges of O atoms are more dispersive distributed due to the conjugation of ethynyl phenothiazine. In the meanwhile, the negative charges of N atoms in the D−A molecules increase a lot, accompanied by the augment of the positive charges of S atoms. The larger difference between the atomic charges of N and S in the conjugated D−A compounds may lead to higher ground-state dipole moment (3.86 D for AqMp, 3.93 D for Aq_2Mp) relative to the parent Mp molecule (2.46 D). So it can be inferred that intramolecular interaction exists between the donor and acceptor in the two D−A compounds.

Overall, the DFT and TDDFT calculations on the two compounds discussed above provide deep insight into their electronic structures and properties.

Conclusions

In summary, two conjugated D−A compounds with different chromophores using phenothiazine as donor, anthraquinone as acceptor, and ethynylene as linker are successfully synthesized by Sonogashira coupling reactions. The structural effect on their optical and electrochemical properties is investigated. DFT and TDDFT calculations have allowed a detailed understanding of the electronic structure and absorption spectra of the two compounds. The DFT calculations showed that the HOMOs and LUMOs of the two molecules are highly localized on the donor and acceptor moieties, respectively, and better coplanarity and π-electron conjugation is found in the frontier orbitals of compound Aq_2Mp. The different coplanarity, π-electron conjugation, DFT-calculated energy levels of frontier orbitals and HOMO−LUMO energy gaps of the two compounds are in excellent agreement with their experimental optical and electrochemical results. Moreover, it could be deduced that better coplanarity and larger conjugated effect may lead to lower HOMO−LUMO gaps.

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Supporting Information Available: Plots of some other frontier orbitals of AqMp and Aq_2Mp (Figure S1 and Figure S2), the results of TDDFT calculations for Aq and Mp (Figure S3, Figure S4, Table S1 and Table S2). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 402. (b) Chen, C. H.; Shi, J.; Tang, C. W.; Klubek, K. P. *Thin Solid Films* **2000**, *363*, 327. (c) Li, J. Y.; Liu, D.; Hong, Z. R.; Tong, S. W.; Wang, P. F.; Ma, C. W.; Lengyel, O.; Lee, C. S.; Kwong, H. L.; Lee, S. T. *Chem. Mater.* **2003**, *15*, 1486. (d) Thomas, K. R. J.; Lin, J. T.; Velusamy, M.; Tao, Y.-T.; Chuen, C.-H. *Adv. Funct. Mater.* **2004**, *14*, 83.

(2) (a) Mitschke, U.; Bauerle, P. *J. Mater. Chem.* **2000**, *10*, 1471. (b) Tao, X. T.; Miyata, S.; Sasabe, H.; Zhang, G. J.; Wada, T.; Jiang, M. H. *Appl. Phys. Lett.* **2001**, *78*, 279. (c) Kulkarni, A. P.; Tonzola, C. J.; Babel, A.; Jenekhe, S. A. *Chem. Mater.* **2004**, *16*, 4556. (d) Chiang, C.-L.; Wu, M.-F.; Dai, D.-C.; Wen, Y.-S.; Wang, J.-K.; Chen, C.-T. *Adv. Funct. Mater.* **2005**, *15*, 231.

(3) (a) Richter, M. M.; Fan, F. F.; Klavetter, F.; Heeger, A. J.; Bard, A. J. *Chem. Phys. Lett.* **1994**, *226*, 115. (b) Lai, R. Y.; Fabrizio, E. F.; Lu, L.; Jenekhe, S. A.; Bard, A. J. *J. Am. Chem. Soc.* **2001**, *123*, 9112. (c) Richter, M. M. *Chem. Rev.* **2004**, *104*, 3003. (d) Dini, D. *Chem. Mater.* **2005**, *17*, 1933. (e) Kulkarni, A. P.; Wu, P.-T.; Kwon, T. W.; Jenekhe, S. A. *J. Phys. Chem. B* **2005**, *109*, 19584.

(4) (a) Armstrong, N. R.; Wightman, R. M.; Gross, E. M. *Annu. Rev. Phys. Chem.* **2001**, *52*, 391. (b) Janakiraman, U.; Doblhofer, K.; Fischmeister, C.; Holmes, A. B. *J. Phys. Chem. B* **2004**, *108*, 14368. (c) Fungo, F.; Wong, K.-T.; Ku, S.-Y.; Hung, Y.-Y.; Bard, A. J. *J. Phys. Chem. B* **2005**, *109*, 3984. (d) Kulkarni, A. P.; Zhu, Y.; Babel, A.; Wu, P.-T.; Jenekhe, S. A. *Chem. Mater.* **2008**, *20*, 4212.

(5) (a) Wong, M. S.; Li, Z. H.; Tao, Y.; D'Iorio, M. *Chem. Mater.* **2003**, *15*, 1198. (b) Loi, M. A.; Denk, P.; Hoppe, H.; Neugebauer, H.; Winder, C.; Meissner, D.; Brabec, C.; Sariciftci, N. S.; Gouloumis, A.; Vazquezb, P.; Torresb, T. *J. Mater. Chem.* **2003**, *13*, 700. (c) Sun, X.; Liu, Y.; Xu, X.; Yang, C.; Yu, G.; Chen, S.; Zhao, Z.; Qiu, W.; Li, Y.; Zhu, D. *J. Phys. Chem. B* **2005**, *109*, 10786.

(6) Jiao, G. S.; Thoresen, L. H.; Burgess, K. *J. Am. Chem. Soc.* **2003**, *125*, 14668.

(7) (a) Albota, M.; Beljonne, D.; Bredas, J. L.; Ehrlich, J. E.; Fu, J. Y.; Heikal, A. A.; Hess, S. E.; Kogej, T.; Levin, M. D.; Marder, S. R.; Perry, J. W.; Rockel, H.; Rumi, M.; Subramaniam, G.; Webb, W. W.; Wu, X. L.; Xu, C. *Science* **1998**, *281*, 1653. (b) Staub, K.; Levina, G. A.; Barlow, S.; Kowalczyk, T. C.; Lackritz, H. S.; Barzoukas, M.; Fortd, A.; Marder, S. R. *J. Mater. Chem.* **2003**, *13*, 825. (c) Abbotto, A.; Beverina, L.; Bozio, R.; Facchetti, A.; Ferrante, C.; Pagani, G. A.; Pedron, D.; Signorini, R. *Chem. Commun.* **2003**, 2144.

(8) (a) Hamada, Y.; Adachi, C.; Tsutsui, T.; Saito, S. *Jpn. J. Appl. Phys.* **1992**, *31*, 1812. (b) Tamoto, N.; Adachi, C.; Nagai, K. *Chem. Mater.* **1997**, *9*, 1077. (c) Antoniadis, H.; Inbasekaran, M.; Woo, E. P. *Appl. Phys. Lett.* **1998**, *73*, 3055. (d) Tao, Y.-T.; Chuen, C.-H.; Ko, C. W.; Peng, J. W. *Chem. Mater.* **2002**, *14*, 4256. (e) Thomas, K. R. J.; Lin, J. T.; Velusamy, M.; Tao, Y.-T.; Chuen, C.-H. *Adv. Funct. Mater.* **2004**, *14*, 83. (f) Zhang, H.; Huo, C.; Zhang, J.; Zhang, P.; Tian, W.; Wang, Y. *Chem. Commun.* **2006**, 281. (g) Hancock, J. M.; Gifford, A. P.; Zhu, Y.; Lou, Y.; Jenekhe, S. A. *Chem. Mater.* **2006**, *18*, 4924.

(9) (a) Jenekhe, S. A.; Lu, L.; Alam, M. M. *Macromolecules* **2001**, *34*, 7315. (b) Zhu, W.; Hu, M.; Yao, R.; Tian, H. *J. Photochem. Photobiol. A* **2003**, *154*, 169. (c) Kulkarni, A. P.; Kong, X.; Jenekhe, S. A. *Adv. Funct. Mater.* **2006**, *16*, 1057.

(10) (a) Antoniadis, H.; Inbasekaran, M.; Woo, E. P. *Appl. Phys. Lett.* **1998**, *73*, 3055. (b) Li, Z. H.; Wong, M. S.; Fukutani, H.; Tao, Y. *Org. Lett.* **2006**, *8*, 4271. (c) Chen, C.-T.; Wei, Y.; Lin, J.-S.; Moturu, M. V. R. K.; Chao, W.-S.; Tao, Y.-T.; Chien, C.-H. *J. Am. Chem. Soc.* **2006**, *128*, 10992. (d) Zhu, Y.; Gibbons, K. M.; Kulkarni, A. P.; Jenekhe, S. A. *Macromolecules* **2007**, *40*, 804.

(11) (a) Oseki, Y.; Fujitsuka, M.; Cho, D. W.; Sugimoto, A.; Tojo, S.; Majima, T. *J. Phys. Chem. B* **2005**, *109*, 19257. (b) Perepichka, I. F.; Perepichka, D. F.; Meng, H.; Wudl, F. *Adv. Mater.* **2005**, *17*, 2281. (c) Nishizawa, T.; Tajima, K.; Hashimoto, K. *J. Mater. Chem.* **2007**, *17*, 2440. (d) Murphy, A. R.; Frechet, J. M. J. *Chem. Rev.* **2007**, *107*, 1066.

(12) (a) Hamada, Y.; Adachi, C.; Tsutsui, T.; Saito, S. *Jpn. J. Appl. Phys.* **1992**, *31*, 1812. (b) Tamoto, N.; Adachi, C.; Nagai, K. *Chem. Mater.* **1997**, *9*, 1077. (c) Thomas, K. R. J.; Lin, J. T.; Tao, Y.-T.; Chuen, C.-H. *Chem. Mater.* **2002**, *14*, 3852. (d) Xiang, N. J.; Lee, T. H.; Gong, M. L.; Tong, K. L.; So, S. K.; Leung, L. M. *Synth. Met.* **2006**, *156*, 270.

(13) (a) Shirota, Y.; Kinoshita, M.; Noda, T.; Okumoto, T.; Ohara, T. *J. Am. Chem. Soc.* **2000**, *122*, 11021. (b) Doi, H.; Kinoshita, M.; Okumoto, K.; Shirota, Y. *Chem. Mater.* **2003**, *15*, 1080. (c) Zhang, H.; Huo, C.; Zhang, J.; Zhang, P.; Tian, W.; Wang, Y. *Chem. Commun.* **2006**, 281.

(14) Oh, J.-J.; Kim, K.-W.; Kim, M.-S.; Kwon, T.-W.; Park, D.-K.; Cho, S.-J.; Woo, H.-S. *Appl. Phys. Lett.* **2006**, *89*, 073504.

(15) Thomas, K. R. J.; Lin, J. T.; Tao, Y.-T.; Chuen, C.-H. *J. Mater. Chem.* **2002**, *12*, 3516.

(16) (a) Zhu, Y.; Champion, R. D.; Jenekhe, S. A. *Macromolecules* **2006**, *39*, 8712. (b) Xia, Y.; Luo, J.; Deng, X.; Li, X.; Li, D.; Zhu, X.; Yang, W.; Cao, Y. *Macromol. Chem. Phys.* **2006**, *207*, 511.

(17) (a) Shi, C.; Yao, Y.; Yang, Y.; Pei, Q. *J. Am. Chem. Soc.* **2006**, *128*, 8980. (b) Hou, Q.; Zhou, Q.; Zhang, Y.; Yang, W.; Yang, R.; Cao, Y. *Macromolecules* **2004**, *37*, 6299. (c) Zhu, Z.; Waller, D.; Gaudiana, R.; Morana, M.; Mülhlbacher, D.; Scharber, M.; Brabec, C. *Macromolecules* **2007**, *40*, 1981. (d) Huo, L.; He, C.; Han, M.; Zhou, E.; Li, Y. F. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 3861.

(18) (a) Liu, Y.; Cao, H.; Li, J.; Chen, Z.; Cao, S.; Xiao, L.; Xu, S.; Gong, Q. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 4867. (b) Yang, L. Y.; Wang, C.; Li, L. Q.; Janietz, S.; Wedel, A.; Hua, Y. L.; Yin, S. G. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 4291. (c) Park, M.-J.; Lee, J.; Park, J.-H.; Lee, S. K.; Lee, J.-I.; Chu, H.-Y.; Hwang, D.-H.; Shim, H.-K. *Macromolecules* **2008**, *41*, 3063.

(19) Zou, Y.; Wu, W.; Sang, G.; Yang, Y.; Liu, Y.; Li, Y. *Macromolecules* **2007**, *40*, 7231.

(20) (a) Cho, N. S.; Park, J. H.; Lee, S. K.; Lee, J.; Shim, H. K. *Macromolecules* **2006**, *39*, 177. (b) Tang, W.; Kietzke, T.; Vemulamada, P.; Chen, Z. K. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 5266. (c) Li, K.-C.; Hsu, Y.-C.; Lin, J.-T.; Yang, C.-C.; Wei, K.-H.; Lin, H.-C. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 4285.

(21) (a) Mietzsch, F. *Angew. Chem.* **1954**, *66*, 363. (b) Ionescu, M.; Mantsch, H. *Adv. Heterocycl. Chem.* **1967**, *8*, 83. (c) Bodea, C.; Silberg, I. *Adv. Heterocycl. Chem.* **1968**, *9*, 321. (d) Okafor, C. O. *Heterocycles* **1977**, *7*, 391. (e) Albery, W. J.; Foulds, A. W.; Hall, K. J.; Hillman, A. R.; Edgell, R. G.; Orchard, A. F. *Nature* **1979**, *282*, 793. (f) Kristiansen, J. E.; Mortensen, I. *Pharmacol. Toxicol.* **1987**, *60*, 100. (g) Mazumder, R.; Ganguly, K.; Dastidar, S. G.; Chakrabarty, A. N. *Int. J. Antimicrob. Agents* **2001**, *18*, 403.

(22) (a) Amaral, L.; Kristiansen, J. E. *Int. J. Antimicrob. Agents* **2001**, *18*, 411. (b) Korth, C.; May, B. C.; Cohen, F. E.; Prusiner, S. B. *Proc. Natl. Acad. Sci. U.S.A.* **2001**, *98*, 9836.

(23) (a) Kristiansen, J. E.; Hansen, J. B. *Int. J. Antimicrob. Agents* **2000**, *14*, 209. (b) Lind, K. E.; Du, Z.; Fujinaga, K.; Peterlin, B. M.; James, T. L. *Chem. Biol.* **2002**, *9*, 185. (c) Kristiansen, J. E.; Hansen, J. B. *J. Am. Chem. Soc.* **2004**, *126*, 4453. (d) Mayer, M.; Lang, P. T.; Gerber, S.; Madrid, P. B.; Pinto, I. G.; R.; Guy, K.; James, T. L. *Chem. Bio.* **2006**, *13*, 993.

(24) (a) Wasielewski, M. R. *Chem. Rev.* **1992**, *34*, 435. (b) Kurreck, H.; Huber, M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 849. (c) Murata, M.; Yamada, M.; Fujita, T.; Kojima, K.; Kurihara, M.; Kubo, K.; Kobayashi, Y.; Nishihara, H. *J. Am. Chem. Soc.* **2001**, *123*, 12903. (d) Gouloumis, A.; González-Rodrıguez, D.; Vázquez, P.; Torres, T.; Liu, S.; Echegoyen, L.; Ramey, J.; Hug, G. L.; Guldi, D. M. *J. Am. Chem. Soc.* **2006**, *128*, 12674. (e) Kondo, M.; Uchikawa, M.; Zhang, W.-W.; Namiki, K.; Kume, S.; Murata, M.; Kobayashi, Y.; Nishihara, H. *Angew. Chem., Int. Ed.* **2007**, *46*, 6271.

(25) (a) Breslin, D. T.; Schuster, G. B. *J. Am. Chem. Soc.* **1996**, *118*, 2311. (b) Schuster, G. B. *Acc. Chem. Res.* **2000**, *33*, 253. (c) Asche, C. *Mini Rev. Med. Chem.* **2005**, *5*, 449. (d) Pors, K.; Shnyder, S. D.; Teesdale-Spittle, P. H.; Hartley, J. A.; Zloh, M.; Searcey, M.; Patterson, L. H. *J. Med. Chem.* **2006**, *49*, 7013. (e) Bergeron, F.; Nair, V. K.; Wagner, J. R. *J. Am. Chem. Soc.* **2006**, *128*, 14798. (g) Srinivas, G.; Babykutty, S.; Sathiadevan, P. P.; Srinivas, P. *Med. Res. Rev.* **2007**, *27*, 591.

(26) Kim, S. K.; Lee, J. H.; Hwang, D. H. *Synth. Met.* **2005**, *152*, 201.

(27) (a) Cymerman-Craig, J.; Rogers, W. P.; Warwick, G. P. *Aust. J. Chem.* **1955**, *8*, 252. (b) Bodea, C.; Terdic, M. *Acad. Rep. Pop. Rom.* **1962**, *13*, 81 Chem. Abstr. 1963, 59, 11477b.

(28) (a) Müller, T. J. J. *Tetrahedron Lett.* **1999**, *40*, 6563. 2. Krämer, C. S.; Müller, T. J. J. *Eur. J. Org. Chem.* **2003**, 3534.

(29) *Methoden der Organischen Chemie*; Müller, E., Bayer, O., Eds.; Thieme: Stuttgart, 1979; Vol. 4, Chapter VII/3c, p 54.

(30) 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, R.; 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.; Bakken, V.; 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 B.04; Gaussian, Inc.: Wallingford, CT, 2004.

(31) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(32) (a) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (b) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200.

(33) Kuboyama, A.; Matauzaki, S.; Takagi, H.; Arano, H. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 1604.

(34) (a) Lai, R. Y.; Kong, X.; Jenekhe, S. A.; Bard, A. J. *J. Am. Chem. Soc.* **2003**, *125*, 12631. (b) Zhang, W. W.; Yu, Y. G.; Lu, Z. D.; Mao, W. L.; Li, Y. Z.; Meng, Q. J. *Organometallics* **2007**, *26*, 865.

(35) (a) Gupta, N.; Linschitz, H. *J. Am. Chem. Soc.* **1997**, *119*, 6384. (b) Murata, M.; Fujita, T.; Yamada, M.; Kurihara, M.; Nishihara, H. *Chem. Lett.* **2000**, 1328.

(36) Daub, J.; Engl, R.; Kurzawa, J.; Miller, S. E.; Schneider, S.; Stockmann, A.; Wasielewski, M. R. *J. Phys. Chem. A* **2001**, *105*, 5655.

(37) Sailer, M.; Nonnenmacher, M.; Oeser, T.; Müller, T. J. J. *Eur. J. Org. Chem.* **2006**, 423.

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