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Unsymmetrical and Symmetrical Push−Pull Phenothiazines

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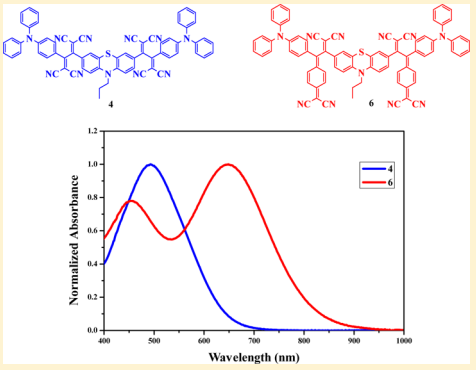
Supporting Information

ABSTRACT: A series of unsymmetrical and symmetrical push−pull phenothiazines (**3**−**7**) were designed and synthesized by the Pd-catalyzed Sonogashira cross-coupling reaction and subsequent [2 + 2] cycloaddition−retroelectrocyclization reaction with tetracyanoethylene (TCNE) and 7,7,8,8-tetracyanoquinodimethane (TCNQ). The effect of systematic variation of the number and nature of cyano-based acceptor TCNE and TCNQ units on the photophysical, electrochemical, and computational studies was investigated. The single-photon absorption on phenothiazines **3**−**7** reveals that substitution of 1,1,4,4-tetracyanobutadiene (TCBD) and a cyclohexa-2,5-diene-1,4-diylidene-expanded TCBD unit results in strong intramolecular charge transfer and lowering of the LUMO energy level. The TCBD-linked and cyclohexa-2,5-diene-1,4-diylidene-expanded TCBD-linked phenothiazines **3**−**7** exhibit multi-redox waves. The computational studies on phenothiazines **3**−**7** exhibit substantial stabilization of the LUMO with the increase in acceptor strength, which results in lowering of the HOMO−LUMO gap.



INTRODUCTION

The precise tuning of photonic and electronic properties of π-conjugated donor−acceptor (D−A) systems is essential for efficient optoelectronic applications.[1−4] These properties in turn are function of the LUMO energy level and can be perturbed either by altering the strength of D/A units or by varying the π-linker.[5,6] Recently, cross-conjugation has been utilized as a facile methodology to tune the LUMO energy level with a varying number of electron acceptors.[7,8] The cross-conjugated systems based on 1,1,4,4-tetracyanobutadiene (TCBD) and cyclohexa-2,5-diene-1,4-diylidene-expanded TCBD electron-withdrawing groups have emerged as promising candidates in organic electronics.[9,10] The substitution of the TCBD and cyclohexa-2,5-diene-1,4-diylidene-expanded TCBD unit in π-conjugated systems have been achieved via [2 + 2] cycloaddition−retroelectrocyclization between donor-substituted alkynes and tetracyanoethylene (TCNE)/7,7,8,8-tetracyanoquinodimethane (TCNQ).[11] The TCBD-based and cyclohexa-2,5-diene-1,4-diylidene-expanded TCBD-based D−A systems exhibit intense intramolecular charge transfer (ICT) interactions and broad absorption.[12] Our group and others have explored TCBD and cyclohexa-2,5-diene-1,4-diylidene-expanded TCBD-substituted D−A polymers and small molecules for nonlinear optics and organic photovoltaics.[13,14]

Phenothiazine belongs to an important class of tricyclic heterocycles. The phenothiazine ring containing electron-rich sulfur and nitrogen atoms exhibits nonplanar geometry and good thermal and electrochemical stability.[15,16] Müller et al. have designed and synthesized a variety of phenothiazines derivatives.[17] Recently, phenothiazine-based small molecules have been explored for organic photovoltaics.[18] We were interested in incorporating the triphenylamine donor and systematically altering the TCNE/TCNQ acceptor on the phenothiazine to see its effect on the photonic properties.

In this paper, we wish to report unsymmetrical and symmetrical phenothiazines **3**−**7** synthesized via the [2 + 2] cycloaddition−retroelectrocyclization reaction. In order to investigate the systematic variation of the acceptor unit on the photophysical properties and HOMO−LUMO gap, we have varied the acceptor from mono-TCBD/cyclohexa-2,5-diene-1,4-diylidene-expanded TCBD to di-TCBD/cyclohexa-2,5-diene-1,4-diylidene-expanded TCBD in phenothiazines **3**−**6**. We have also synthesized phenothiazine **7** with TCNE and TCNQ acceptor incorporated together in a single molecular system. The photophysical, electrochemical, and computational studies on phenothiazines **3**−**7** were performed to study the effect of enhanced π-conjugation and the acceptor strength of TCBD/cyclohexa-2,5-diene-1,4-diylidene-expanded TCBD derivatives.

RESULT AND DISCUSSION

The synthesis of triphenylamine-functionalized phenothiazines **2**−**7** are shown in Schemes 1 and 2. The dibromophenothiazine **1** was synthesized following earlier reports [Scheme S1, Supporting Information (SI)].[19,20] The Sonogashira cross-coupling reactions of dibromophenothiazine **1** with 2.1 equiv of 4-ethynyl-*N*,*N*-diphenylaniline resulted in symmetrical phenothiazine **2** in 70% yield.[21] The [2 + 2] cycloaddition−retroelectrocyclization reaction of phenothiazine **2** with TCNE and TCNQ resulted in TCBD/cyclohexa-2,5-diene-

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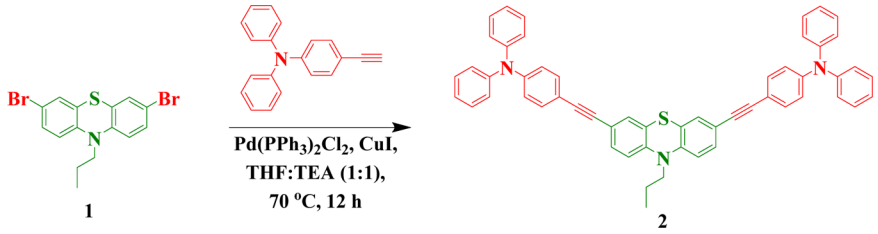
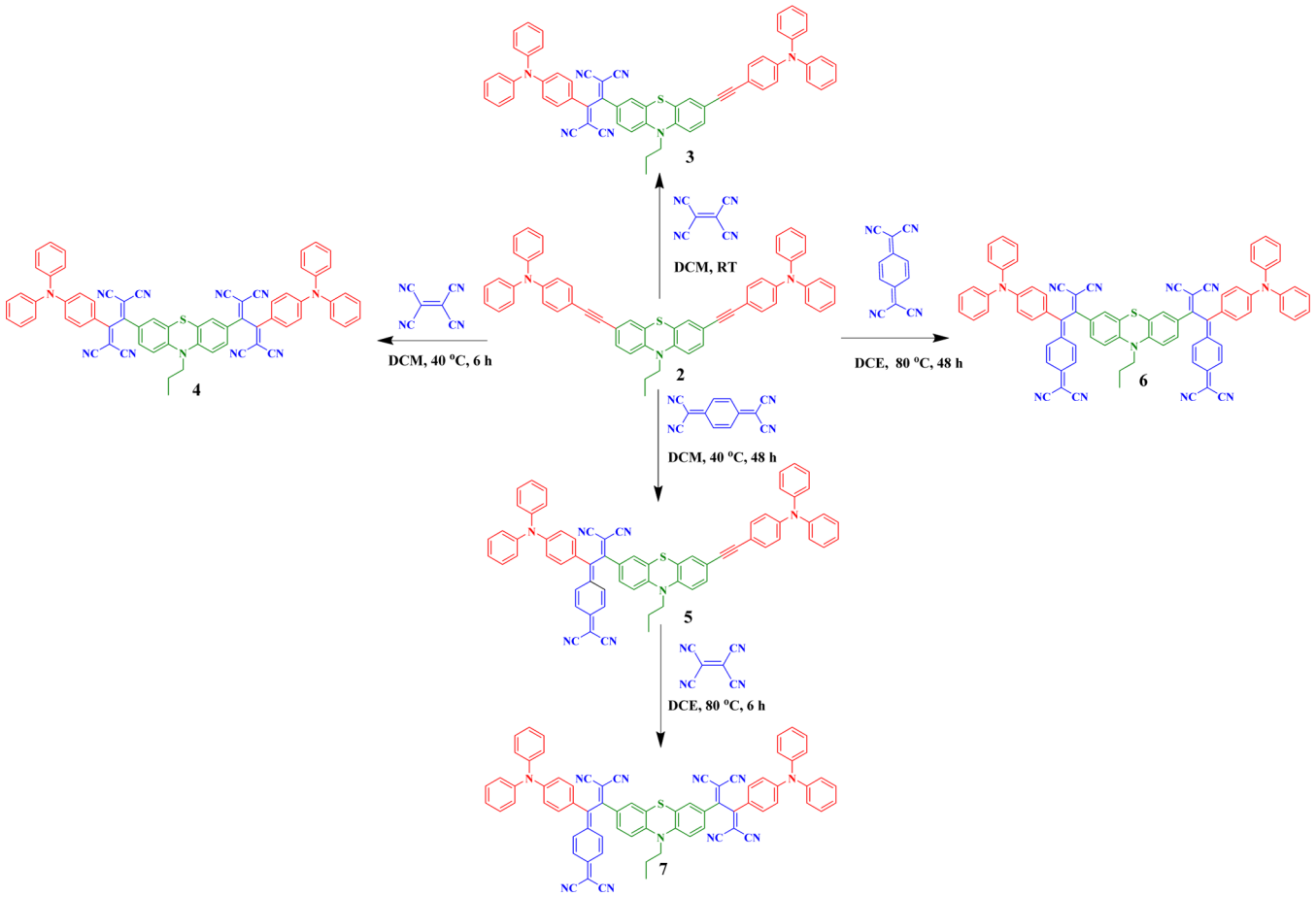
Scheme 1. Synthesis of Phenothiazine 2



Scheme 2. Synthesis of Triphenylamine-Substituted TCBD/Cyclohexa-2,5-diene-1,4-diylidene-Expanded TCBD Phenothiazines 3−7



1,4-diylidene-expanded TCBD-functionalized phenothiazines **3**−**7** [Scheme 2 and Scheme S1 (SI)].

The reaction of 1.1 equiv of TCNE with phenothiazine **2** in dichloromethane (DCM) at room temperature resulted in phenothiazine **3** in 90% yield, whereas the reaction of 2 equiv of TCNE with phenothiazine **2** at 40 °C resulted in phenothiazine **4** in 90% yield.[22] The unsymmetrical phenothiazine **5** was obtained in 30% yield upon reaction of 1 equiv of TCNQ with phenothiazine **2** in dichloromethane at 40 °C. The [2 + 2] cycloaddition−retroelectrocyclization reaction of phenothiazine **2** with 2 equiv of TCNQ at 80 °C in dichloroethane (DCE) resulted in phenothiazine **6** in 50% yield. The phenothiazine **7** was synthesized from phenothiazine **2** in two steps. The initial step involved the synthesis of phenothiazine **5**, which upon reaction with 1 equiv of TCNE in dichloroethane at 80 °C resulted in phenothiazine **7** in 85% yield. We also synthesized phenothiazine **7** from phenothiazine **3** with the addition of 1 equiv of TCNQ in dichloroethane at 80 °C in 83% yield (Scheme S1, SI).

The purification of the phenothiazines **3**−**7** was achieved by column chromatography, and all the compounds were well-characterized by ^{1}H and ^{13}C NMR and HRMS techniques.

Photophysical Properties. The electronic absorption spectra of unsymmetrical and symmetrical phenothiazines **3**−**7** were recorded in dichloromethane at room temperature (Figure 1), and the data are compiled in Table 1. The absorption spectra of phenothiazines **3** and **4** exhibit a strong ICT band at 498 and 492 nm, which can be attributed to the strong donor−acceptor interaction resulting from the incorporation of the tetracyanobutadiene acceptor unit, which was further explained by TD−DFT calculation on the dichloromethane phase. The disubstituted TCBD phenothiazine **4** shows a blue shift of 6 nm as compared to monosubstituted TCBD phenothiazine **3**.

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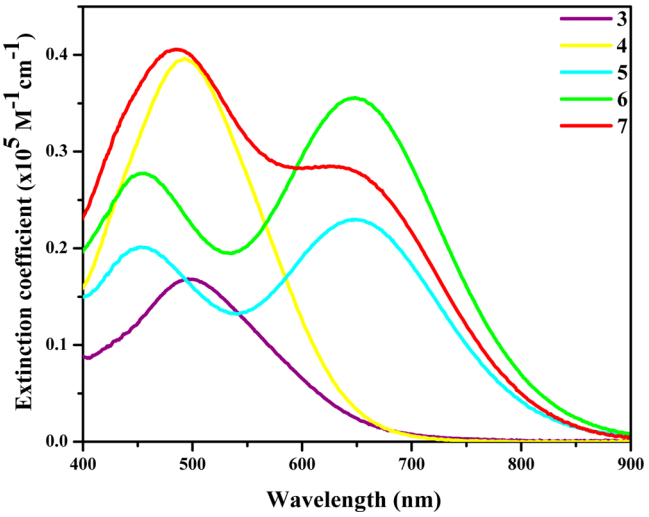

Figure 1. Absorption spectra of phenothiazines **3**–**7** in dichloromethane (1×10^{-5} M).

Table 1. Photophysical and Electrochemical Data of Unsymmetrical and Symmetrical Phenothiazines 3–7

	photophysical data[a]			electrochemical data[b]	
compd	λ_{abs} (nm)	ε (M^{-1} cm^{-1})	optical band gap (eV)	E_{ox} (V)	E_{red} (V)
3	498	17 000	1.83	0.76	−0.58
				0.89	−0.88
				1.08	
4	492	40 000	1.9	1.10	−0.52
					−0.87
5	450	20 000	1.47	0.67	−0.45
				0.79	
	648	23 000		1.06	−0.55
6	453	28 000	1.45	0.77	−0.37
7	650	36 000		0.90	−0.49
	483	41 000	1.49	0.79	−0.37
	636	28 000		0.97	−0.48
					−0.64
					−0.93

[a]Absorbance measured in dichloromethane at 1×10^{-5} M concentration. λ_{abs}: absorption wavelength. ε: extinction coefficient. [b]Electrochemical analysis was estimated by differential pulse voltammetry, in 0.1 M solution of $TBAPF_6$ in DCM at 100 mV s^{-1} scan rate versus SCE electrode.

The phenothiazines **5** and **6** exhibit a π–π^* transition at 450 and 453 nm and an intramolecular charge transfer (ICT) transition at ∼648 and ∼650 nm, respectively. Similarly, phenothiazine **7** exhibits a π–π^* transition at 483 nm and an intramolecular charge transfer (ICT) transition at ∼636 nm. The incorporation of the TCBD/cyclohexa-2,5-diene-1,4-diylidene-expanded TCBD acceptor unit results in a considerable red shift of the onset absorption wavelength.[10i] The absorption spectra of cyclohexa-2,5-diene-1,4-diylidene-expanded TCBD-functionalized phenothiazines **5** and **6** show a large bathochromic shift of ∼150 nm as compared to TCBD-functionalized phenothiazines **3** and **4**, due to the strong electron-accepting character of the cyclohexa-2,5-diene-1,4-diylidene-expanded TCBD moiety.

The optical energy gap of phenothiazines **3**–**7** was estimated from the onset edge of the absorption spectra in dichloromethane and exhibits the order **4** > **3** > **7** > **5** > **6**. The observed trend shows that the optical energy gap in these systems is a function of the nature and number of acceptor units. The computational studies explain all these transitions by TD–DFT calculation.

Electrochemical Properties. The electrochemical properties of phenothiazines **3**–**7** were explored by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in dry DCM solution at room temperature using 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as a supporting electrolyte with glassy carbon as the working electrode, Pt wire as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. The electrochemical data are compiled in Table 1, and the representative cyclic voltammograms and differential pulse voltammograms of phenothiazines **3**–**7** are shown in Figure 2 and Figure S20 (SI).

The phenothiazines **3** and **5** exhibit a reversible two-step reduction wave attributed to one-electron transfer in each step, the reduction potentials were identified by DPV as (−0.58, −0.88 V) and (−0.45, −0.55 V).[10e,25] The TCBD-functionalized and cyclohexa-2,5-diene-1,4-diylidene-expanded TCBD-functionalized phenothiazines **4** and **6** show a two-step reduction wave, and the potentials identified at (−0.52, −0.87 V) and (−0.52, −1.19 V) are associated with two-electron transfer in each step to form a tetraanionic species.[10e,11,13a] The comparison of the first reduction potential of phenothiazines **3**–**6** reflects that the cyclohexa-2,5-diene-1,4-diylidene-expanded TCBD-linked phenothiazines **5** and **6** are easier to reduce than TCBD-linked phenothiazines **3** and **4**, which can be attributed to the strong electron-accepting nature of the cyclohexa-2,5-diene-1,4-diylidene-expanded TCBD unit.[10i,25]

The TCBD and cyclohexa-2,5-diene-1,4-diylidene-expanded TCBD adduct of phenothiazine **7** exhibits four reduction waves at −0.37, −0.48, −0.64, and −1.16 V to form tetraanionic species.[25] The phenothiazines **3** and **5** exhibit three oxidation waves, whereas phenothiazines **6** and **7** exhibit two oxidation waves attributed to the phenothiazine and the triphenylamine moiety.[23,24,26] The phenothiazine **4** shows one oxidation wave due to the simultaneous oxidation of the phenothiazine and triphenylamine units. The electrochemical HOMO and LUMO energy levels were estimated from the onset oxidation and reduction potential.[12a,14] The corresponding HOMO and LUMO energy levels of phenothiazines **3**–**7** are −5.11, −5.43, −5.11, −5.07, and −5.05 eV and −3.90, −3.94, −4.08, −4.05, and −4.07 eV, respectively.

Theoretical Calculations. In order to explore the effect of acceptors' strength on the electronic structure and stabilization of the LUMO energy level of the unsymmetrical and symmetrical phenothiazines **3**–**7**, density functional theory (DFT) calculations were performed at the B3LYP/6-31G** level.[27] The frontier molecular orbitals are outlined in Figure S23 (SI).

The optimized structures of phenothiazines **3**–**7** are nonplanar with a twisted backbone due to incorporation of TCBD and cyclohexa-2,5-diene-1,4-diylidene-expanded TCBD units. The HOMOs are mainly localized on the triphenylamine unit, whereas LUMOs are concentrated on TCBD and cyclohexa-2,5-diene-1,4-diylidene-expanded TCBD units for phenothiazines **3**–**7**, resulting a strong charge transfer from the triphenylamine unit to TCBD and the cyclohexa-2,5-diene-1,4-diylidene-expanded TCBD unit.[10i] The LUMO orbital of phenothiazine **7** is mainly localized on the cyclohexa-2,5-diene-

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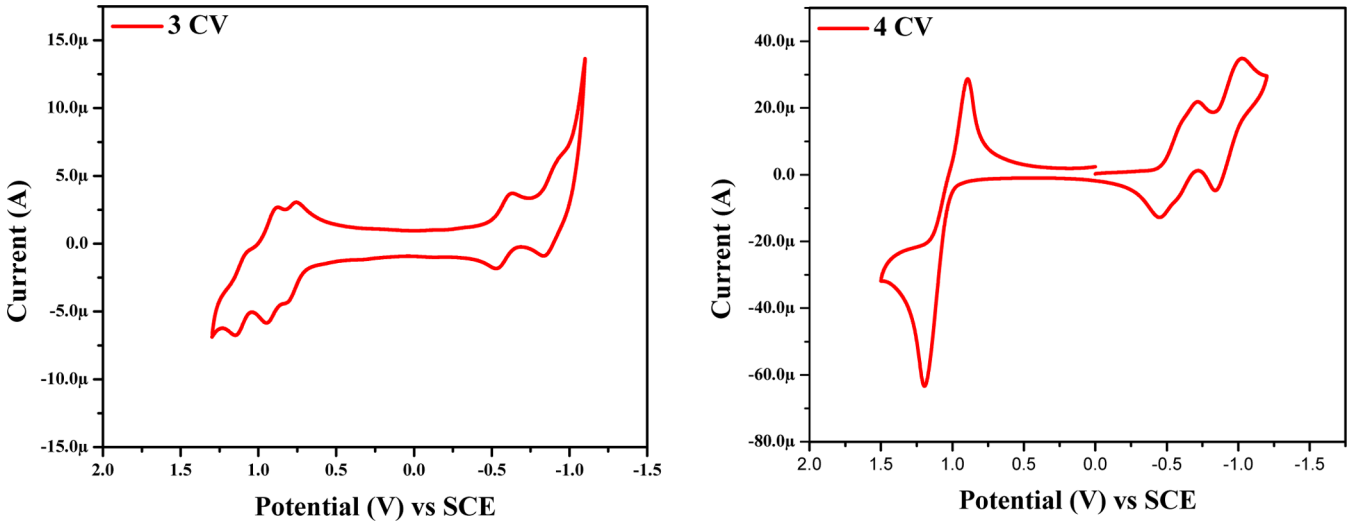

Figure 2. Cyclic voltammograms of phenothiazines **3** and **4** in 0.1 M solution of Bu_4NPF_6 in dichloromethane at 100 mV s^{-1} scan rate versus saturated calomel electrode (SCE) at 25 °C.

1,4-diylidene-expanded TCBD moiety, which signifies that the cyclohexa-2,5-diene-1,4-diylidene-expanded TCBD moiety is a stronger acceptor than TCBD.

The energy level diagrams of the frontier molecular orbitals are shown in Figure 3. The theoretically estimated HOMO

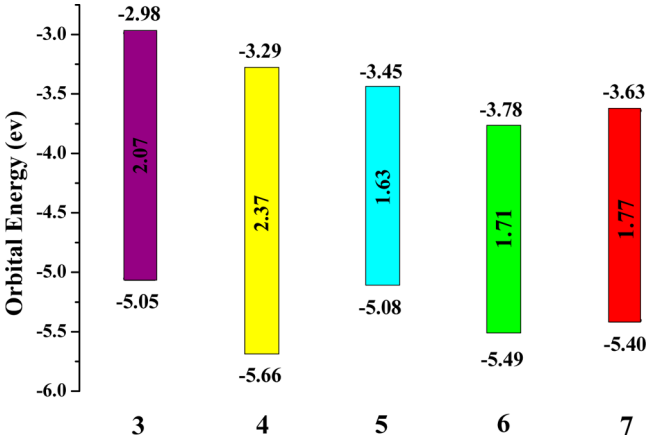

Figure 3. Energy levels diagram of the frontier orbitals of phenothiazines **3**–**7** estimated by DFT calculations.

levels for the phenothiazines **3**–**7** are −5.05, −5.66, −5.08, −5.49, and −5.40 eV and the corresponding LUMO levels are −2.98, −3.29, −3.45, −3.78, and −3.63 eV, respectively.

The incorporation of the strong acceptors TCBD and cyclohexa-2,5-diene-1,4-diylidene-expanded TCBD units lower the LUMO energy level, which results in a red shift in the electronic absorption. The trend in the LUMO energy level of phenothiazines **3**–**6** follows the order **3** > **4** > **5** > **6**, which exhibits that the LUMO energy level is decreasing with an increase in the strength and number of acceptors (TCBD and cyclohexa-2,5-diene-1,4-diylidene-expanded TCBD units) Figure 3.

The time-dependent DFT calculation was performed at the B3LYP/6-31G(d,p) level on optimized phenothiazines **3** and **4** and the CAM-B3LYP/6-31G(d,p) level on optimized phenothiazines **5**–**7** in dichloromethane to calculate the transitions involved in the electronic absorption spectra. The transitions with composition, oscillator strengths, and assignments are shown in Table 2. The TD-DFT calculations show a single absorption band due to intramolecular charge transfer (ICT) at 486 and 493 nm, respectively, for phenothiazines **3** and **4**, whereas the phenothiazines **5**–**7** exhibit two absorption bands in the visible region.

The phenothiazines **5**, **6**, and **7** exhibit π–π^* transition at 335, 370, and 439 nm in the lower wavelength region and intramolecular charge transfer (ICT) at 574, 581, and 620 nm in the longer wavelength region, respectively.[23,24] In experimental as well as theoretical UV/vis spectra, phenothiazines **3** and **4** exhibit one electronic transition that corresponds to intramolecular charge transfer (ICT), whereas phenothiazines **5**–**7** exhibit two electronic transitions related to π–π^* and

Table 2. Calculated Electronic Transitions for Phenothiazines 3–7 in Dichloromethane

phenothiazine	wavelength (nm)	composition and molecular contribution	f^a	assignment
3	486	HOMO−1 → LUMO+1 (75%)	0.25	ICT
4	493	HOMO−2→LUMO+2 (24%)	0.57	ICT
5	574	HOMO−1→LUMO (93%)	1.17	ICT
	335	HOMO→LUMO+2 (63%)	0.86	π–π^*
6	581	HOMO→LUMO (58%)	1.38	ICT
	370	HOMO−2→LUMO+2 (67%)	0.28	π–π^*
7	620	HOMO→LUMO (95%)	1.06	ICT
	439	HOMO−1→LUMO+2 (9%)	0.61	π–π^*

[a]Oscillator strength.

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intramolecular charge transfer (ICT) transitions in the visible region.

CONCLUSION

In summary, a series of donor−acceptor aryl-substituted unsymmetrical and symmetrical phenothiazines derivatives **3**−**7** were synthesized by the Pd-catalyzed Sonogashira cross-coupling reaction and subsequent [2 + 2] cycloaddition−retroelectrocyclization reactions. The results show that the incorporation of TCBD and cyclohexa-2,5-diene-1,4-diylidene-expanded TCBD acceptor groups perturb the LUMO energy level of the phenothiazines to a greater extent. The photophysical and electrochemical properties of phenothiazine derivatives **3**−**7** exhibit strong ICT at longer wavelength.

EXPERIMENTAL SECTION

Experimental Details. Chemicals were used as received unless otherwise indicated. All the oxygen- or moisture-sensitive reactions were carried out under an argon atmosphere. ^{1}H NMR spectra were recorded using a 400 MHz spectrometer. Chemical shifts are reported in δ units, expressed in parts per million (ppm) downfield from tetramethylsilane (TMS) using residual protonated solvent as an internal standard ($CDCl_3$, 7.27 ppm). ^{13}C NMR spectra were recorded using a 100 MHz spectrometer. Chemical shifts are reported in δ units, expressed in parts per million (ppm) downfield from tetramethylsilane (TMS) using the solvent as internal standard ($CDCl_3$, 77.0 ppm). The ^{1}H NMR splitting patterns have been described as s, singlet; d, doublet; t, triplet; and m, multiplet. UV−visible absorption spectra of all compounds were recorded in dichloromethane solution. Cyclic voltammograms and differential pulse voltammograms were recorded on a potentiostat using glassy carbon as the working electrode, Pt wire as the counter electrode, and a SCE as the reference electrode. The scan rate was 100 mV s^{-1} for cyclic voltammetry. A solution of $TBAPF_6$ in DCM (0.1 M) was used as the supporting electrolyte.

*2-(4-(Diphenylamino)phenyl)-3-(7-((4-(diphenylamino)phenyl)-ethynyl)-10-propyl-10H-phenothiazin-3-yl)buta-1,3-diene-1,1,4,4-tetracarbonitrile (Phenothiazine **3**).* In a 100 mL round bottomed flask, TCNE (63 mg, 1 mmol) was added to a solution of compound phenothiazine **2** (387 mg, 1 mmol) in CH_2Cl_2 (50 mL) under an argon atmosphere. The mixture was heated at 30 °C for 6 h. The solvent was removed in vacuum, and the product was purified by SiO_2 column chromatography with DCM/hexane (2:1, v/v) as eluent to yield phenothiazine **3** as a dark brown solid (406 mg, yield 90%): mp 155.3−183.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75−7.72 (m, 1H), 7.65 (d, J = 9.04 Hz, 2H), 7.40 (t, J = 8.0 Hz, 4H), 7.35−7.28 (m, 8H), 7.23−7.18 (m, 6H), 7.12−7.05 (m, 6H),7.01−6.99 (d, J = 8.5 Hz, 2H), 6.93−6.91 (d, J = 9.0 Hz, 2H), 6.87−6.80 (m, 3H), 3.84 (t, J = 7.5 Hz, 2H), 2.33 (m, 2H), 1.05 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 164.1, 153.7, 150.3, 148.0, 147.1, 144.5, 141.5, 132.4, 131.8, 130.0, 129.4, 127.8, 126.9, 126.6, 125.2, 125.0, 123.6, 122.7, 122.1, 119.8, 118.0, 115.8, 115.1, 112.9,112.7, 90.7, 87.1, 81.1, 50.0, 19.9, 11.0; HRMS (ESI-TOF) m/z calcd for $C_{61}H_{41}N_7S$ + Na 926.3036 [M + Na]$^+$, measured 926.3128 [M + Na]$^+$.

*3,3′-(10-Propyl-10H-phenothiazine-3,7-diyl)bis(2-(4-(diphenylamino)phenyl)buta-1,3-diene-1,1,4,4-tetracarbonitrile) (Phenothiazine **4**).* In a 100 mL round bottomed flask, TCNE (130 mg, 1 mmol)) was added to a solution of phenothiazine **2** (387 mg 0.50 mmol) in CH_2Cl_2 (50 mL) under an argon atmosphere. The mixture was heated at 40 °C for 6 h. After cooling to room temperature, the solvent was removed under vacuum and the product was purified by silica gel column chromatography with DCM/hexane (2:1, v/v) as eluent to yield phenothiazine **4** as a dark brown solid (463 mg, yield 90%): mp 173.2−195.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.7 Hz, 2H), 7.65 (d, J = 8.5 Hz, 4H,), 7.41 (t, J = 7.0 Hz, 9H), 7.29−7.22 (m, 12H), 6.94 (t, J = 5.5 Hz, 7H), 3.88 (t, J = 6.7 Hz, 2H), 1.89−1.84 (m, 2H), 1.07 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 163.3, 153.8, 148.0, 144.3, 131.8, 130.4, 130.0, 127.8, 126.9, 126.8, 124.3, 121.0, 117.9, 116.0, 113.5, 112.8, 112.3, 111.6, 83.5, 50.2, 19.8, 11.0; HRMS (ESI-TOF) m/z calcd for $C_{67}H_{41}N_{11}S$ + Na 1054.3159 [M + Na]$^+$, measured 1054.3160 [M + Na]$^+$.

*2-(4-(3,3-Dicyano-1-(4-(diphenylamino)phenyl)-2-(7-((4-(diphenylamino)phenyl)ethynyl)-10-propyl-10H-phenothiazin-3-yl)-allylidene)cyclohexa-2,5-dien-1-ylidene)malononitrile (Phenothiazine **5**).* In a 100 mL round bottomed flask TCNQ (150 mg, 1.5 mmol) was added to a solution of compound **2** (387 mg, 1 mmol) in CH_2Cl_2 (50 mL). The mixture was heated at 40 °C for 48 h. After cooling to room temperature, the solvents were removed under vacuum, and the product was purified by silica gel column chromatography with DCM as the eluent to yield phenothiazine **5** as a dark-colored solid (362 mg, yield 74%): mp 187.4−205.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 8.52 Hz, 1H), 7.55 (d, J = 9.04 Hz, 1H), 7.39−7.28 (m, 12H), 7.21−7.17 (m, 10H), 7.12−7.07 (m,7H), 7.01−6.94 (m, 5H), 6.81 (t, J = 10.0 Hz, 2H), 3.82 (t, J = 5.5 Hz, 2H), 1.86−1.81 (m, 2H), 1.04 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 154.0, 151.5, 150.9, 149.7, 148.0, 147.0, 145.3, 141.7, 135.1, 134.2, 133.2, 132.4, 130.9, 130.3, 130.0, 129.8, 129.3, 128.3, 127.8, 126.9, 126.5, 125.8, 125.7, 125.5,125.0, 124.7, 123.6, 122.7, 122.1, 119.6, 119.2, 115.7, 115.5, 115.0, 114.1, 114.1, 113.6, 112.9, 90.7, 87.1, 82.1, 74.0, 49.8, 19.9, 11.0; HRMS (ESI-TOF) m/z calcd for $C_{67}H_{45}N_7S$ + Na 1002.3349 [M + Na]$^+$, measured 1002.3340 [M + Na]$^+$.

*2,2′-((10-Propyl-10H-phenothiazine-3,7-diyl)bis(2-(4-(dicyanomethylene)cyclohexa-2,5-dien-1-ylidene)-2-(4-(diphenylamino)phenyl)ethan-1-yl-1-ylidene))dimalononitrile (Phenothiazine **6**).* In a 100 mL round bottomed flask, TCNQ (200 mg, 1 mmol) was added to a solution of compound **2** (387 mg, 0.50 mmol) in DCE (50 mL). The mixture was heated at 80 °C for 48 h. After cooling to room temperature, the solvents were removed under vacuum, and the product was purified by silica gel column chromatography with DCM as the eluent to yield phenothiazine **6** as a dark-colored solid (296 mg, yield 50%): mp >250.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56−7.51 (m, 4H), 7.38 (t, 8H), 7.32−7.30 (m, 3H), 7.24−7.14 (m, 19H), 6.98−6.84 (m, 8H), 3.81 (t, J = 7.0 Hz, 2H), 1.86−1.80 (m, 2H), 1.05 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 153.9, 151.6, 150.0, 147,4, 145.2, 135.0, 133.9, 133.2, 132.3, 130.5, 129.9, 129.3, 128.0, 126.6, 126.0, 125.6, 124.0, 119.2, 115.7, 114.0, 113.2, 112.4, 84.2, 74.4, 50.3, 19.8, 11.0; HRMS (ESI-TOF) m/z calcd for $C_{79}H_{49}N_{11}S$ + Na 1206.3575 [M + Na]$^+$, measured 1206.3785 [M + Na]$^+$.

*2-(7-(1,1-Dicyano-3-(4-(dicyanomethylene)cyclohexa-2,5-dien-1-ylidene)-3-(4-(diphenylamino)phenyl)prop-1-en-2-yl)-10-propyl-10H-phenothiazin-3-yl)-3-(4-(diphenylamino)phenyl)buta-1,3-diene-1,1,4,4-tetracarbonitrile (Phenothiazine **7**).* In a 100 mL round bottomed flask, TCNQ (100 mg, 1 mmol) was added to a solution of phenothiazine **2** (387 mg, 1 mmol) in $C_2H_4Cl_2$ (50 mL). The mixture was heated at 80 °C for 48 h. After that TCNE (63 mg, 1 mmol) was added to a solution of compound phenothiazine **5** (489 mg, 1 mmol) in DCE (50 mL). The mixture was refluxed at 80 °C for 6 h. The solvent was removed in vacuum, and the product was purified by SiO_2 column chromatography with DCM as the eluent to yield phenothiazine **7** as a dark-colored solid (0.47 g, yield 85%): mp 185.5−215.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (7.72−7.55 (m, 6H), 7.44−7.38 (m, 9H), 7.33−7.29 (m, 6H), 7.24−7.17 (m, 10H), 7.01−6.91 (m, 7H), 3.87 (t, J = 8.0 Hz, 2H), 1.90−1.85 (m, 2H), 1.09 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 165.3, 163.4, 153.9, 151.6, 150.0, 148.1, 147.3, 145.2, 144.3, 135.0, 133.2, 132.3, 131.8, 130.5, 130.3, 130.1, 129.9, 129.4, 128.2, 127.7, 126.9, 126.8, 126.7, 126.6, 125.9, 125.9, 125.7, 124.2, 121.1, 119.2, 117.9, 115.9, 114.0, 113.1, 112.8, 112.4, 111.6, 84.2, 83.4, 77.5, 74.4, 50.3, 29.6, 11.0; HRMS (ESI-TOF) m/z calcd for $C_{73}H_{45}N_{11}S$ + Na 1130.3472 [M + Na]$^+$, measured 1130.3475 [M + Na]$^+$.

ASSOCIATED CONTENT

Supporting Information

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^{1}H and ^{13}C NMR and HRMS spectra of all the new compounds, cyclic voltammograms, and computational results (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Parker, T. C.; Patel, D. G.; Moudgil, K.; Barlow, S.; Risko, C.; Brédas, J.-L.; Reynolds, J. R.; Marder, S. R. *Mater. Horiz.* **2015**, *2*, 22.

(2) Ricks, A. B.; Solomon, G. C.; Colvin, M. T.; Scott, A. M.; Chen, K.; Ratner, M. A.; Wasielewski, M. R. *J. Am. Chem. Soc.* **2010**, *132*, 15427.

(3) Roncali, J. *Macromol. Rapid Commun.* **2007**, *28*, 1761.

(4) Bureš, F. *RSC Adv.* **2014**, *4*, 58826.

(5) (a) Cao, D.; Peng, J.; Hong, Y.; Fang, X.; Wang, L.; Meier, H. *Org. Lett.* **2011**, *13*, 1610. (b) Bodedla, G. B.; Thomas, K. R. J.; Li, C. T.; Ho, K. C. *RSC Adv.* **2014**, *4*, 53588. (c) Hauck, M.; Schönhaber, J.; Zucchero, A. J.; Hardcastle, K. I.; Müller, T. J. J.; Bunz, U. H. F. *J. Org. Chem.* **2007**, *72*, 6714.

(6) (a) Kulkarni, A. P.; Wu, P. T.; Kwon, T. W.; Jenekhe, S. A. *J. Phys. Chem. B* **2005**, *109*, 19584. (b) Konidena, R. K.; Thomas, K. R. J.; Kumar, S.; Wang, Y. C.; Li, C.-J.; Jou, J.-H. *J. Org. Chem.* **2015**, *80*, 5812.

(7) (a) Leu, W. C. W.; Hartley, C. S. *Org. Lett.* **2013**, *15*, 3762. (b) Kivala, M.; Diederich, F. *Acc. Chem. Res.* **2009**, *42*, 235.

(8) (a) Gholami, M.; Tykwinski, R. R. *Chem. Rev.* **2006**, *106*, 4997. (b) Zucchero, A. J.; McGrier, P. L.; Bunz, U. H. F. *Acc. Chem. Res.* **2010**, *43*, 397.

(9) (a) Michinobu, T.; May, J. C.; Lim, J. H.; Boudon, C.; Gisselbrecht, J.-P.; Seiler, P.; Gross, M.; Biaggio, I.; Diederich, F. *Chem. Commun.* **2005**, 737. (b) Michinobu, T. *Chem. Soc. Rev.* **2011**, *40*, 2306. (c) Shoji, T.; Maruyama, M.; Ito, S.; Morita, N. *Bull. Chem. Soc. Jpn.* **2012**, *85*, 761−773. (d) Shoji, T.; Ito, S.; Okujima, T.; Morita, N. *Chem. - Eur. J.* **2013**, *19*, 5721−5730. (e) Shoji, T.; Maruyama, M.; Shimomura, E.; Maruyama, A.; Ito, S.; Okujima, T.; Toyota, K.; Morita, N. *J. Org. Chem.* **2013**, *78*, 12513−12524. (f) Reutenauer, P.; Kivala, M.; Jarowski, P. D.; Boudon, C.; Gisselbrecht, J−P.; Gross, M.; Diederich, F. *Chem. Commun.* **2007**, 4898−4900.

(10) (a) Esembeson, B.; Scimeca, M. L.; Michinobu, T.; Diederich, F.; Biaggio, I. *Adv. Mater.* **2008**, *20*, 4584. (b) Pokladek, Z.; Ripoche, N.; Betou, M.; Trolez, Y.; Mongin, O.; Olesiak-Banska, J.; Matczyszyn, K.; Samoc, M.; Humphrey, M. G.; Blanchard-Desce, M.; Paul, F. *Chem. - Eur. J.* **2016**, *22*, 10155. (c) Michinobu, T. *Pure Appl. Chem.* **2010**, *82*, 1001−1009. (d) Shoji, T.; Ito, S.; Toyota, K.; Yasunami, M.; Morita, N. *Chem. - Eur. J.* **2008**, *14*, 8398−8408. (e) Shoji, T.; Ito, S.; Toyota, K.; Iwamoto, T.; Yasunami, M.; Morita, N. *Eur. J. Org. Chem.* **2009**, *2009*, 4316−4324. (f) Yamada, M.; Schweizer, W. B.; Schoenebeck, F.; Diederich, F. *Chem. Commun.* **2010**, *46*, 5334−5336. (g) Jordan, M.; Kivala, M.; Boudon, C.; Gisselbrecht, J.-P.; Schweizer, W. B.; Seiler, P.; Diederich, F. *Chem. - Asian J.* **2011**, *6*, 396−401. (h) Kivala, M.; Boudon, C.; Gisselbrecht, J.-P.; Seiler, P.; Gross, M.; Diederich, F. *Chem. Commun.* **2007**, 4731−4733. (i) Shoji, T.; Maruyama, M.; Shimomura, E.; Maruyama, A.; Ito, S.; Okujima, T.; Toyota, K.; Morita, N. *J. Org. Chem.* **2013**, *78*, 12513−12524.

(11) Shoji, T.; Ito, S.; Okujima, T.; Morita, N. *Org. Biomol. Chem.* **2012**, *10*, 8308.

(12) (a) Gautam, P.; Misra, R.; Siddiqui, S. A.; Sharma, G. D. *ACS Appl. Mater. Interfaces* **2015**, *7*, 10283. (b) Patil, Y.; Misra, R.; Keshtov, M. L.; Sharma, G. D. *J. Phys. Chem. C* **2016**, *120*, 6324.

(13) (a) Leliège, A.; Blanchard, P.; Rousseau, T.; Roncali, J. *Org. Lett.* **2011**, *13*, 3098−3101. (b) Michinobu, T.; Satoh, N.; Cai, J.; Li, Y.; Han, L. *J. Mater. Chem. C* **2014**, *2*, 3367−3372.

(14) Zhang, H.; Wan, X.; Xue, X.; Li, Y.; Yu, A.; Chen, Y. *Eur. J. Org. Chem.* **2010**, *2010*, 1681−1687.

(15) (a) Hart, A. S.; K C, C. B.; Subbaiyan, N. K.; Karr, P. A.; D'Souza, F. *ACS Appl. Mater. Interfaces* **2012**, *4*, 5813. (b) Kim, M.-J.; Yu, Y.-J.; Kim, J.-H.; Jung, Y.-S.; Kay, K.-Y.; Ko, S.-B.; Lee, C.-R.; Jang, I.-H.; Kwon, Y.-U.; Park, N.-G. *Dyes Pigm.* **2012**, *95*, 134.

(16) Chang, Y. J.; Chou, P.-T.; Lin, Y.-Z.; Watanabe, M.; Yang, C.-J.; Chin, T.-M.; Chow, T. J. *J. Mater. Chem.* **2012**, *22*, 21704.

(17) (a) Krämer, C. S.; Zeitler, K.; Müller, T. J. J. *Org. Lett.* **2000**, *2*, 3723. (b) Sailer, M.; Nonnenmacher, M.; Oeser, T.; Müller, T. J. J. *Eur. J. Org. Chem.* **2006**, *2006*, 423. (c) Sailer, M.; Rominger, F.; Müller, T. J. J. *J. Organomet. Chem.* **2006**, *691*, 299. (d) Memminger, K.; Oeser, T.; Müller, T. J. J. *Org. Lett.* **2008**, *10*, 2797−2800. (e) Hauck, M.; Turdean, R.; Memminger, K.; Schönhaber, J.; Rominger, F.; Müller, T. J. J. *J. Org. Chem.* **2010**, *75*, 8591.

(18) (a) Hua, Y.; Chang, S.; Huang, D.; Zhou, X.; Zhu, X.; Zhao, J.; Chen, T.; Wong, W.-K.; Wong, W.-Y. *Chem. Mater.* **2013**, *25*, 2146. (b) Baheti, A.; Thomas, K. R. J.; Li, C.-T.; Lee, C.-P.; Ho, K.-C. *ACS Appl. Mater. Interfaces* **2015**, *7*, 2249. (c) Sharma, G. D.; Anil Reddy, M.; Ramana, D. V.; Chandrasekharam, M. *RSC Adv.* **2014**, *4*, 33279. (d) Tan, Q.; Yang, X.; Cheng, M.; Wang, H.; Wang, X.; Sun, L. *J. Phys. Chem. C* **2014**, *118*, 16851.

(19) (a) Kim, S. H.; Kim, H. W.; Sakong, C.; Namgoong, J.; Park, S. W.; Ko, M. J.; Lee, C. H.; Lee, W. I.; Kim, J. P. *Org. Lett.* **2011**, *13*, 5784−5787. (b) Sanap, A. K.; Sanap, K. K.; Shankarling, G. S. *Dyes Pigm.* **2015**, *120*, 190−199. (c) Zheng, M.; Sun, M.; Li, Y.; Wang, J.; Bu, L.; Xue, S.; Yang, W. *Dyes Pigm.* **2014**, *102*, 29−34.

(20) Bieliauskas, A.; Martynaitis, V.; Getautis, V.; Malinauskas, T.; Jankauskas, V.; Kamarauskas, E.; Holzer, W.; Šačkus, A. *Tetrahedron* **2012**, *68*, 3552−3559.

(21) Gautam, P.; Maragani, R.; Misra, R. *RSC Adv.* **2015**, *5*, 18288.

(22) Misra, R.; Gautam, P.; Maragani, R. *Tetrahedron Lett.* **2015**, *56*, 1664.

(23) Zhang, W.-W.; Yu, Y.-G.; Lu, Z.-D.; Mao, W.-L.; Li, Y.-Z.; Meng, Q.-J. *Organometallics* **2007**, *26*, 865−873.

(24) Zhang, W.-W.; Mao, W.-Li; Hu, Y.-X.; Tian, Z.-Q.; Wang, Z.-L.; Meng, Q.-J. *J. Phys. Chem. A* **2009**, *113*, 9997.

(25) Misra, R.; Gautam, P. *Org. Biomol. Chem.* **2014**, *12*, 5448−5457.

(26) Kivala, M.; Boudon, C.; Gisselbrecht, J.-P.; Seiler, P.; Gross, M.; Diederich, F. *Angew. Chem.* **2007**, *119*, 6473.

(27) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; 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.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09, revision A.02*; Gaussian, Inc., Wallingford, CT, 2009.

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