ORGANIC
LETTERS

2012
Vol. 14, No. 6
1588–1591

Charge-Transfer Properties of Lateral Triphenylamine–Dithienophosphole Diads

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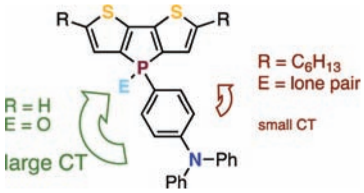
Received February 9, 2012

ABSTRACT



Installation of an exocyclic triphenylamine group at the phosphorus center provides access to dithienophosphole materials with lateral charge-transfer (CT) ability. The degree of CT can be significantly manipulated not only via oxidation of the P-center but also surprisingly by alkylation of the 2,6-position of the scaffold.

Due to the steadily growing impact of organic electronics, the development of new π-conjugated chromophores continues to be an important area of research.[1] A vast array of systems has been developed that, among other features, quite efficiently addresses not only the light-emitting and the redox properties of the materials but also the transfer of energy and charges. In the context of charge-transfer (CT) phenomena, there has been a lot of interest in the photophysical properties of donor–acceptor (D–A) systems linked by a single bond.[2] Others and we recently established that organophosphorus-based conjugated materials exhibit pronounced electron-accepting features[3] that naturally lend themselves to be utilized in such D–A systems. Notably, the acceptor character of phosphorus can significantly be increased through simple oxidation of this center.[3] While it has been shown that the longitudinal installation of donor groups at the periphery of phosphorus-based conjugated systems can lead to some intriguing photophysical properties,[4] the effect of exocyclic donor substitutents as a lateral component in a D–A architecture is virtually unexplored for these systems.[5] However, the pyramidal geometry of the P-center is particuarly intriguing in this context, as it could intrinsically lead to some interesting properties.[4] In this contribution we now report the synthesis and characterization of novel D–A

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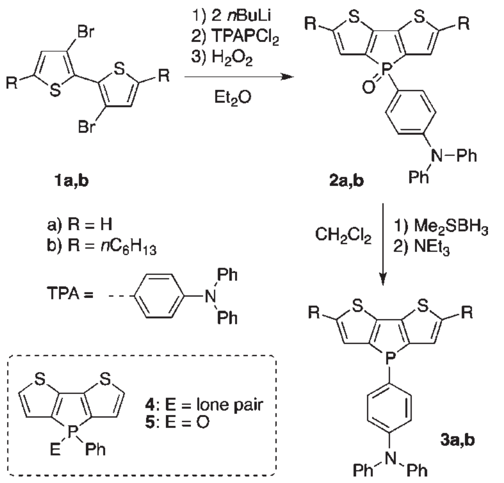
10.1021/ol300331f

systems, in which our trademark dithienophosphole unit constitutes the acceptor component, and an exocyclic triphenylamine species acts as the donor. Our study addresses the charge-transfer properties of the system via modification of the phosphorus center, as well as the 2,6-position of the dithienophosphole scaffold; the experimental data are further supported by theoretical calculations.

The synthetic strategy involved the corresponding 3,3′-dibromo-2,2′-bithiophenes **1a,b** that were lithiated with *n*BuLi *in situ*, followed by the addition 4-*N*,*N*-diphenylaminophenylphosphorus dichloride (TPAPCl$_2$) at low temperature. For purification purposes, the trivalent compounds were immediately oxidized with excess H$_2$O$_2$, providing **2a** and **2b** in 48% and 49% yields after column chromatography, respectively (Scheme 1).

Scheme 1. Synthesis of the TPA-Functionalized Dithieno[3,2-*b*:2′,3′-*d*]phospholes



In order to obtain the trivalent species, the pentavalent species **2a,b** were treated with a slight excess of borane (from BH$_3$SMe$_2$), followed by the addition of excess NEt$_3$ to provide the corresponding phospholes in good yields after workup (**3a** = 68%, **3b** = 81%; Scheme 1).[4e] The trivalent congeners could thereby be obtained in higher purity than via the direct approach.

Compound **2a** was acquired as a light yellow solid showing a ^{31}P{^{1}H} NMR chemical shift at δ = 19.1 ppm, while **2b** was obtained as a dark yellow solid showing a slightly lowfield-shifted ^{31}P NMR resonance at δ = 21.6 ppm, both in a similar range as known dithienophosphole oxides.[4] The compounds showed consistent ^{1}H and ^{13}C NMR data, as well as HRMS and elemental analysis, confirming their identity and purity. The trivalent species exhibited highfield-shifted ^{31}P NMR resonances at δ = -22.4 ppm for the light yellow **3a** and δ = -22.2 ppm for the bright yellow **3b** that clearly confirmed the P-reduced state.[4] Successful formation of the two compounds was further confirmed by ^{1}H and ^{13}C NMR spectra, as well as HRMS analysis.

We were also able to obtain single crystals suitable for X-ray crystallography for **2a** from a concentrated CHCl$_3$ solution upon slow evaporation of the solvent (Figure 1). In general, the bond lengths and angles are in good agreement with previously reported dithienophosphole oxides.[3b,4b,4e] Notably, there is a face-to-face interaction (d = 3.6 Å) between two propeller-shaped TPA units, but no π–π interactions between two neighboring planar dithienophosphole scaffolds are found.

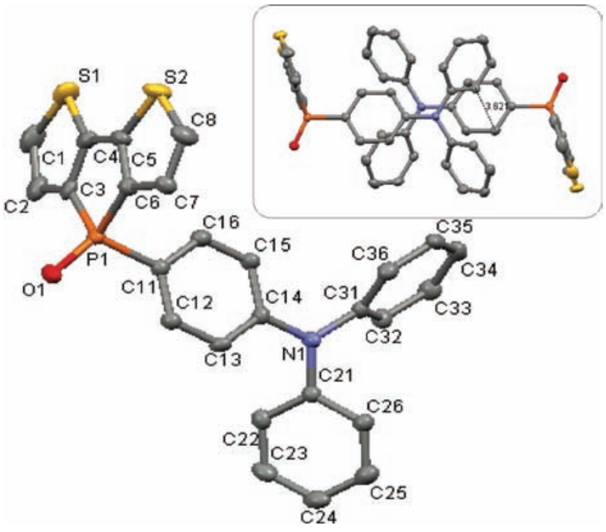


Figure 1. Molecular structure and intermolecular interaction (inset) of **2a** in the solid state (50% probability level, H-atoms are omitted for clarity). Selected bond lengths [Å] and angles [deg]: P1–C3, 1.811(4); P1–C6, 1.802(4); P1–C11, 1.793(4); P1–O1, 1.479(3); C1–C2, 1.372(7); C2–C3, 1.422(6); C3–C4, 1.377(6); C4–C5, 1.463(6); C5–C6, 1.373(5); C6–C7, 1.422(5); C7–C8, 1.360(5); C3–P1–C11, 105.80(17); C6–P1–C11, 104.70(17); C3–P1–O1, 117.80(18); C6–P1–O1, 119.37(17); C11–P1–O1, 114.23(17).

The photophysical properties of the new dithienophospholes were studied in dilute CH$_2$Cl$_2$ solution (~10^{-6} M), and the results are listed in Table 1. It is interesting to note that the pentavalent **2a,b** show similar absorption properties in the typical range for dithienophospholes,[4] while the emission of the H-terminated congener **2a** shows an unexpected red-shifted emission compared to the hexyl-functionalized species at λ_{em} = 508 nm in solution and λ_{em} = 512 nm in the solid state (cf. **2b**: λ_{em} = 472 and 488 nm). ε_{max} values for the two compounds range between 16 000 and 18 000 L mol^{-1} cm^{-1}, which is similar to previously reported dithienophospholes.[6] The Stokes shifts on the other hand range from 8700 to 9900 cm^{-1} and are larger than those of the literature-reported dithienophospholes.[6] In turn, the photoluminescence quantum yields of **2a,b** at ϕ_{PL} = 0.16 and 0.18, respectively, are comparatively low.[4,6] The trivalent compounds **3a,b** have similar absorption and

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Table 1. Photophysical and Electrochemical Properties of the TPA-Functionalized Dithienophospholes

compd	λ_{abs} [nm][a]	ε_{max} [L mol^{-1}cm^{-1}][b]	λ_{em} [nm][c]	Stokes shift [cm^{-1}]	ϕ_{PL}[d]	λ_{ex} (solid) [nm]	λ_{em} (solid) [nm]	E_{red} [V][e]	E_{ox} [V][e]
2a	304, **338**	16 000	508	9900	0.16	403	512	–1.35	0.71
2b	289, **335**	18 000	472	8700	0.18	441	488	–1.31	0.71
3a	**319**	6900	431	8100	0.04	374	467	–	0.60, 1.02
3b	**318**	7200	434	8400	0.08	370	469	–	0.57, 1.00

[a] UV/vis absorption maxima in CH_2Cl_2. [b] Extinction coefficient from λ_{max} (bold values). [c] Emission maxima in CH_2Cl_2, excitation at respective $\pi-\pi^*$ transitions. [d] Photoluminescence quantum yields in CH_2Cl_2, relative to quinine sulfate; ± 10%. [e] Peak potentials in CH_3CN vs Fc/Fc^+.

emission wavelengths in solution and the solid state. Both ε_{max} and Stokes shifts for the trivalent species are lower than those of the pentavalent derivatives at 6900–7200 L mol^{-1} cm^{-1} and 8100–8400 cm^{-1}, respectively. The same is true for their quantum yields at ϕ_{PL} = 0.04 for **3a** and ϕ_{PL} = 0.08 for **3b**. Judging by the observed absorption and emission wavelengths, the dithienophosphole appears to remain the main chromophore in these diads, but the low quantum yields and large Stokes shifts indicate that the origin of the lowest energy transitions are indeed CT processes.[2,4]

To further gauge the suitability of the system for the desired CT processes, the electrochemical properties of the TPA-containing dithienophospholes were investigated through cyclic voltammetry (Table 1). Both pentavalent compounds show a similar trend having a quasireversible reduction at $E_{red,peak}$ = −1.35 and −1.31 V for **2a** and **2b**, respectively, in the same range as observed for related dithienophospholes before.[3e] Moreover, the two systems also show a reversible process at $E_{ox,peak}$ = 0.71 V for both species, due to the expected oxidation of the TPA unit.[7a,8] As for the trivalent congeners, no reduction was observed, but both systems exhibit two oxidation peaks: a quasireversible oxidation for the TPA units at $E_{ox,peak}$ = 0.60 V for **3a**, $E_{ox,peak}$ = 0.57 V for **3b**, and an irreversible oxidation at $E_{ox,peak}$ = 1.02 V for **3a**, $E_{ox,peak}$ = 1.00 V for **3b**, due to dithienophosphole oxidation.

A simple but effective way to study CT phenomena is via solvatochromism.[7] The solvents chosen for the study of all four species ranging from the least polar to the most polar with their respective $E_T(30)$[9] values include cyclohexane (CyH: 30.9), diethylether (Et_2O: 34.6), dichloromethane (CH_2Cl_2: 40.7), acetonitrile (CH_3CN: 46.7), and ethanol (EtOH: 51.9). The latter was also used to study the potential effects of hydrogen bonding within the system. A positive solvatochromism was observed for all species and the effect is more pronounced in the emission spectra, as expected.[7,9] Figure 2 summarizes the CT effects on the emission for all four species. Emission of **2b** varies from λ_{em} = 457 nm for the nonpolar CyH to λ_{em} = 480 nm for the polar EtOH. The photoluminescence quantum yields decrease as the polarity increases (CyH: ϕ_{PL} = 0.28; CH_3CN: ϕ_{PL} = 0.06), but the quantum yield in EtOH is realtively high (ϕ_{PL} = 0.15).[4c,10]

Remarkably, **2a** shows a much stronger solvatochromic effect than the alkylated variety. The emission ranges from λ_{em} = 435 nm in CyH all the way to λ_{em} = 560 nm in CH_3CN. The 125 nm differential clearly supports very efficient CT. The quantum yields of **2a** also drastically decrease upon increasing solvent polarity (ϕ_{PL} = 0.23 for CyH; ϕ_{PL} = 0.01 for CH_3CN).

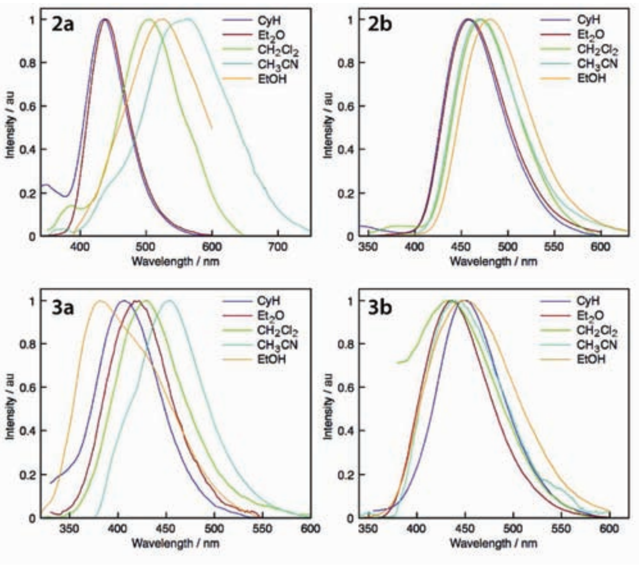

Figure 2. Normalized emission spectra for the solvatochromism of **2a,b** and **3a,b**.

Surprisingly, the red shift in EtOH (λ_{em} = 525 nm) is not as pronounced as would be expected for its high polarity. This observation can be attributed to the hydrogen-bonding capability of EtOH, which evidently impacts the acceptor ability of the dithienophosphole unit, likely

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through interaction with the P-center.[11] The solvatochromic effect for the trivalent system **3b** is smaller than that for its pentavalent counterpart **2b**, in line with the generally reduced acceptor character of the trivalent P-center. Similar to **2a**, the positive solvatochromism of the emission for **3a** from CyH at λ_{em} = 407 nm to CH_3CN at λ_{em} = 453 nm is more pronounced than in the hexyl-substituted congener, but not as pronounced as for its pentavalent relative. Again, the emission in EtOH does not fit the expected trend, as **3a** shows the most blue-shifted emission maximum in this solvent, likely for similar reasons as mentioned for its pentavalent counterpart. In general, the nonalkylated species **2a** and **3a** show more pronounced CT that is probably the result of a more stable charge separated state. The hexyl units apparently impart significant electron density onto the dithienophosphole scaffold making it a much weaker acceptor than the H-substituted relatives.

To support the experimental results, DFT calculations (B3LYP/6-31G(d)) have been performed on the TPA-containing phospholes, their frontier orbital energies and distributions were determined,[12] and TD-DFT was performed to explain dynamic excitation processes (see Supporting Information (SI) for full details). Indeed, the theorectical calculations confirm the observations from the optical spectroscopy studies. The LUMOs of all four species are localized at the dithienophosphole-acceptor end, as expected; however their energies differ substantially as a function of the P-oxidation state and, more importantly, 2,6-substitution, with **2a** showing the lowest energy at $E_L = -1.77$ eV and **3b′** (hexyl truncated with Me) the highest energy at $E_L = -1.13$ eV (cf.: $E_L = -1.65$ eV (**2b′**); $E_L = -1.21$ eV (**3a**)). Furthermore, the HOMOs of the four species mainly show contributions from not only the TPA units but also the dithienophosphole scaffold. However, the latter contribution drops considerably upon moving from **3b′** to **2a**, confirming a concomitant increase in charge separation and CT ability in these systems. Due to the fact that the HOMOs are dominated by the TPA unit, the HOMO energy levels are quite comparable in the four species ranging from $E_H = -4.99$ eV for **3b′** to $E_H = -5.19$ eV for **2a**. TD-DFT confirmed that in all cases the $S_0 \rightarrow S_1$ transitions indeed involve HOMO and LUMO and show relatively low oscillator strengths from $f = 0.006$ to 0.103, supporting their charge-transfer character (see SI). It should be mentioned in this context that while the theoretically obtained wavelengths do not match the experimental values, they nevertheless reproduce a similar trend.

In conclusion, we have developed a synthetic pathway toward laterally functionalized D−A dithienophospholes that show efficient charge transfer from the triphenylamine-donor group to the dithienophosphole-acceptor group, as verified through the study of their solvatochromism and theoretical calculations. Remarkably, the CT character in these species can significantly be enhanced by increasing the acceptor character of the dithienophosphole unit utilizing phosphorus-chemistry approaches, i.e. oxidation from a trivalent to a pentavalent species. More surprisingly however, CT can in turn be noticeably suppressed by installation of simple alkyl substituents at the 2,6-positions of the dithienophosphole scaffold. Based on these initial studies, further development of laterally donor-functionalized dithienophospholes is now underway.

Acknowledgment. Financial support by NSERC of Canada and the Canada Foundation for Innovation (CFI) is gratefully acknowledged. C.J.C. thanks the University of Calgary for an Open scholarship. Y.R. thanks Alberta Ingenuity now part of Alberta Innovates - Technology Futures, and Talisman Energy for graduate scholarships.

Supporting Information Available. Synthetic procedures, NMR spectra, absorption spectra, detailed solvatochromism data, (TD)DFT calculation details, and CV plots for **2a,b** and **3a,b**; CIF file for the X-ray crystallographic data of **2a** (CCDC no.: 866194). This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.