

Communications

D-A-D type molecules based on dibenzophosphole-chalcogenides and triphenylamine moieties; effects of chalcogenide atoms on their photochemical properties

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ABSTRACT: 3,7-bis(4-(diphenylamino)phenyl)-5-phenyl-5*H*-benzo[*b*]phosphinedole 5-sulfide (DBPPS-TPA) and 3,7-bis(4-(diphenylamino)phenyl)-5-phenyl-5*H*-benzo[*b*]phosphinedole 5-selenide (DBPPSe-TPA) are newly synthesized D-A-D type molecules based on dibenzophospholes and their physico-chemical properties are studied in comparison with a P=O type compound, 3,7-bis(4-(diphenylamino)-5-phenyl-5*H*-benzo[*b*]phosphinedole 5-oxide (DBPPO-TPA). Fluorescence emission and electrochemical redox properties of these compounds are investigated regarding results of density functional theory (DFT) calculations, X-ray crystallographic structures and UV-vis absorption spectra. These results exhibit systematic variation in optical properties of these compounds having P=O, P=S, and P=Se units. LUMO energy level is systematically modulated with different chalcogenide atoms.

Heteroles are the widely studied aromatic groups based on five-membered cycles composed of mono-hetero atom and four carbon atoms, such as furan, thiophene, and selenophene. Considerable numbers of heteroles and their derivatives have been synthesized for a building block of various π -conjugated functional molecules and polymers, which are expected to be used as light-emissive materials, electro-conductive materials, and magnetic materials.¹⁻⁵ One of the advantages of the heteroles as the π -building block is their tenability of structural and electronic nature based on the hetero-atoms. For example, its electro-affinity is widely modulated over the isoelectric chemical modification of π -conjugated materials based on the heteroles without significant modulation of their stereo-chemistry. The concept of isoelectric chemical modification of π -conjugated materials based on the heteroles has been expanded into some of oxidized heteroles such as sulfone and sulfoxide even though they are non-aromatic compounds.⁴

Phosphole is composed of phosphorus atom in the five-membered framework and have recently been one of attractive subject in the field of functional π -material chemistry.^{3,6-10} Because of specific coordinating and chalcogen binding nature of phosphorus atom, phosphole acts as a binding site for various heavy atoms.¹¹⁻¹³ Phosphole-chalcogenides can also be the π -building block with isoelectric nature. Since limited number of studies have been conducted for elucidating nature of phosphole-chalcogenides,¹⁴⁻¹⁷ systematic synthetic study on a series of phosphole-chalcogenides and their characterization are still demanded. In the present study, we firstly report on synthesis and photochemical characterization of luminescent molecules based on phosphole-chalcogenides incorporated in a π -conjugated donor-acceptor system.

The synthetic pathways for DBPPS-TPA and DBPPSe-TPA are shown in Chart 1. The precursor of DBPPO-TPA, 3,7-dibromo-5-

phenyl-5*H*-benzo[*b*]phosphinedole 5-oxide, was prepared according to literature method.^{8,18} And also, 4-(diphenylamino)-1-phenylboronic acid as a donor moiety of DBPPO-TPA was prepared according to literature method.¹⁹ The subsequent Suzuki coupling reaction which connected the donor unit with the acceptor unit gave DBPPO-TPA as a precursor of DBPPS-TPA and DBPPSe-TPA. Treatment of DBPPO-TPA with Lawesson's reagent and Woolin's reagent furnished DBPPS-TPA and DBPPSe-TPA, respectively. The DBPPO-TPA has a higher polarity because of phosphole oxide moiety than the DBPPS-TPA and DBPPSe-TPA, and thus these compounds were easily separated from the residual starting material by column chromatography. These compounds were confirmed with ¹H, ¹³C, ³¹P NMR spectra and ESI-HRMS.²⁰

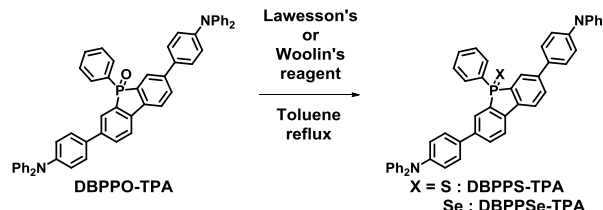


Chart 1. The synthetic pathway for DBPPS-TPA and DBPPSe-TPA

We then elucidated solution phase structure of these compounds with ¹H NMR in CDCl₃. Assignment of these ¹H NMR spectra were determined based on the spectra of precursor.⁸ These ¹H NMR spectra of dibenzophosphole chalcogenides (oxide, sulfide, and selenide) suggested specific intramolecular non-covalent interactions. The proton signal of phenyl group on the phosphorus atom around 7.75 ppm indicated significant low field shift with heavier chalcogen atoms, suggesting hydrogen bond with the chalcogen atom (Figure 1(a)). Although quality of crystals was not enough clear, X-ray crystallographic analysis suggested close contact of the hydrogen and phosphorus atoms (Figure 1(b)).

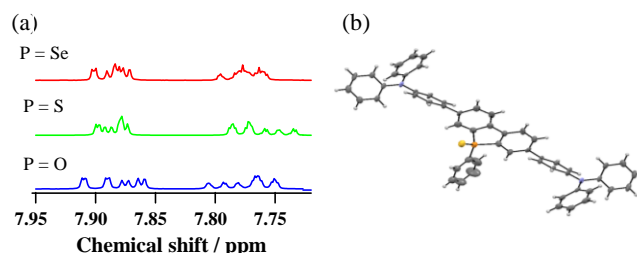


Figure 1. (a) Parts of ¹H NMR spectra in CDCl₃ of these compounds, DBPPO-TPA (blue), DBPPS-TPA (green), and DBPPSe-TPA (red), and (b) ORTEP drawings (showing 50% probability displacement ellipsoids) of the crystal of DBPPS-TPA

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Evaluation of molecular structures and properties of these compounds have performed on the DFT and time-dependent (TD) DFT calculations using Becke three-parameter mixing of exchange and Lee-Yang-Parr correlation functional method (B3LYP) with the 6-311G(d) basis set with Gaussian09 software.²¹ Firstly, we have evaluated the optimized compound geometry in the ground state. Similar structure were obtained for these compounds, in which the single bonds between phenyl groups displayed specific twisting angles between 37.1° to 37.4°. The distance between chalcogen atom and hydrogen of phenyl group was estimated to 0.255 nm (P-O), 0.281 nm (P-S), and 0.288 nm (P-Se), which are shorter than the sum of van der Waals radii of hydrogen (0.120 nm) and chalcogen atoms (O; 0.152 nm, S; 0.180 nm, Se; 0.190 nm). Hydrogen bonding similar to those reported by Zhao and co-workers in dibenzophosphole oxide derivatives²² seems also play dominant role in P=S and P=Se compounds. The phenyl rings connected on the phosphine atoms on these compounds are orthogonally twisted to the dibenzophosphole plane. The LUMOs of these compounds spread on the dibenzophosphole units as the acceptor moiety and the HOMOs are delocalized over entire the molecules excepting for the perpendicularly twisted phenyl groups on the phosphorus atoms (Figure 2).

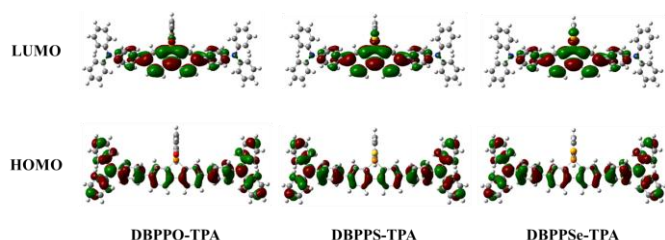


Figure 2. Geometry-optimized structure, and HOMO and LUMO distributions of these compounds calculated at B3LYP/6-311G(d) level.

We then estimated the lowest excited singlet state (E_S) and the lowest excited triplet state (E_T) level by the TD-DFT calculations. Their results summarized in Table 1 with estimated energy of HOMO and LUMO levels. These data showed minor alternation with substituting chalcogen atoms. Slight reduction of the HOMO-LUMO energy gap was observed, 3.28 eV, 3.26 eV, and 3.26 eV for P=O, P=S, and P=Se compounds, respectively, which originates mainly from slight reduction of LUMO energy levels. Smaller E_S and E_T were predicting in compounds with heavy chalcogen atoms. The energy gap between singlet and triplet states also decrease with heavy chalcogen atoms. These tendencies suggest that the compounds with heavy chalcogen atoms could have stronger donor-acceptor nature in the ground and the triplet excited states.

Table 1. Summary of TD-DFT calculations for compounds at the B3LYP/6-311G(d)//B3LYP/6-311G(d) level.^a

Compound	HOMO _{calc} / eV	LUMO _{calc} / eV	E_S / eV	E_T / eV	E_{ST} / eV
DBPPO-TPA	-5.15	-1.87	2.89	2.38	0.51
DBPPS-TPA	-5.16	-1.90	2.88	2.38	0.50
DBPPSe-TPA	-5.16	-1.90	2.86	2.37	0.49

^aHOMO_{calc} and LUMO_{calc}: HOMO and LUMO levels by DFT calculation. E_S and E_T : energy levels of lowest excited singlet and triplet states. E_{ST} : difference between E_S and E_T .

The UV-Vis absorption and photoluminescence spectra of compounds were measured in toluene, chloroform, and acetonitrile and the results are summarized in Figure 3 and Table 2. The UV-Vis absorption spectra indicated similar absorption band and maximum wavelength around 390-400 nm in these conditions. Photoluminescence spectra of these compounds showed similar emission

and maximum wavelength in each solvent. Significant bathochromic-shift of approximately 100 nm was observed in highly polar solvents. We conducted the Lippert-Mataga plot²² for evaluating the solvatochromic Stoke's shift. Clear linear E_T30 dependence of the emission energy, indicated charge transfer (CT) nature of the emissive state. The slopes for DBPPO-TPA, DBPPS-TPA, and DBPPSe-TPA were 13616, 13247, and 13410 cm^{-1} , respectively. Again, little modification of the excited state polarity was induced by exchanging chalcogen atoms on the backbone. Particular attention was paid for photoluminescence quantum yield (PLQY) of DBPPO-TPA and DBPPS-TPA of 89% and 72%, respectively.²⁰ DBPPSe-TPA showed notably lower PLQY. We observed significant difference also in the emission decay profile of those compounds. DBPPO-TPA and DBPPS-TPA indicated well-characterized single exponential emission decay with lifetime of about 1.5 nsec to 4.8 nsec depending on solvent polarity. Meanwhile, DBPPSe-TPA indicated much shorter component in addition to the component of similar lifetime, suggesting branching of excited state reaction pathway. Further characterization is needed to clarify the excited state dynamics of DBPPSe-TPA.

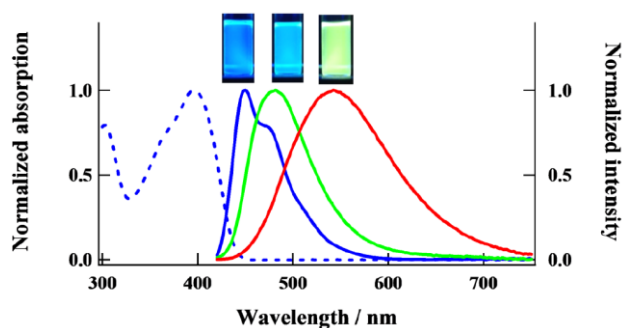


Figure 3. UV-Vis absorption of DBPPS-TPA in toluene (dash line) and photoluminescence (solid line) spectra of DBPPS-TPA in toluene (blue), chloroform (green), and acetonitrile (red) at ambient temperature. Inset: Photographs of UV irradiated solutions of DBPPS-TPA.

Table 2. Summary of the optical properties of these compounds in different solvents at ambient temperature.^a

Compound	Solvent	λ_{abs} / nm	λ_{em} / nm	$\Delta\nu_{ST}$ / cm^{-1}	Φ_F
DBPPO-TPA	toluene	396	451	3100	0.89
	chloroform	399	487	4600	0.83
	acetonitrile	391	545	7300	0.80
DBPPS-TPA	toluene	396	450	3100	0.72
	chloroform	398	481	4300	0.72
	acetonitrile	391	543	7200	0.76
DBPPSe-TPA	toluene	398	449	2800	0.02
	chloroform	399	486	4500	0.05
	acetonitrile	393	550	7200	0.17

^a λ_{abs} : wavelength at UV/Vis absorption maximum. λ_{em} : wavelength at photoluminescence maximum. $\Delta\nu_{ST}$: difference between wavelength at absorption and photoluminescence maximum. Φ_F : photoluminescence quantum yield.

Finally, we evaluated relative potential of HOMO level of these compounds. All these compounds exhibited quasi-reversible oxidation-reduction waves as shown in Figure 4. Table 3 indicates redox potentials of the compound. The clear trends are similar to the results of DFT calculations; higher oxidation potential was observed in the compounds with the heavier chalcogen atoms. Because of spatial distribution of the HOMO state, the oxidation mainly occurs on the π -electron system mainly delocalizing over the diphenylamine units, where the radical spins are regarded to distribute.

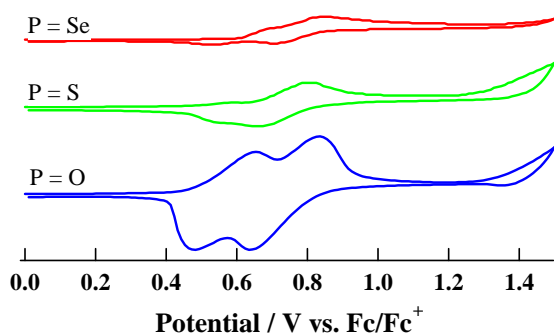


Figure 4. Cyclic voltammograms of these compounds in dichloromethane (scan rate = 0.1 V s^{-1} , conc. = 1 mM, working electrode; Pt wire).

Table 3. Summary of the electrical data of these compounds in dichloromethane at ambient temperature.

Compound	$E_{\text{ox}}^{\text{onset}}$ / eV	$\lambda_{\text{ox}}^{\text{onset}}$ / nm	E_{g} / eV	HOMO _{found} / eV	LUMO _{found} / eV
DBPPO-TPA	0.47	448	2.77	-5.04	-2.27
DBPPS-TPA	0.48	449	2.76	-5.05	-2.29
DBPPSe-TPA	0.60	450	2.76	-5.17	-2.41

In summary, DBPPS-TPA and DBPPSe-TPA are herein newly synthesized with the Lawesson's and Woolin's reagents respectively, and their photoluminescence and electrochemical redox properties are systematically compared with DBPPO-TPA considering the results of DFT calculations. The electron-donating nature of P=X units is softly modulated by chalcogen atoms.

KEYWORDS: photoluminescence, dibenzophosphole, donor-acceptor type π -conjugated molecule

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