### Photophysics

## Thieno[3,4-c]phosphole-4,6-dione: A Versatile Building Block for Phosphorus-Containing Functional $\pi$ -Conjugated Systems

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**Abstract:** A versatile phosphorus-containing  $\pi$ -conjugated thieno[3,4-c]phosphole-4,6-dione building block, (TPHODO), has been developed. The utility of this simple but hitherto unknown building block has been demonstrated by preparing novel functional organophosphorus compounds and bandgap-tunable conjugated polymers.

The incorporation of main-group elements into the main frameworks or the peripherals of  $\pi$ -electron conjugated systems has been emerging as a powerful strategy for the figuration of functional  $\pi$ -conjugated molecules and polymers.<sup>[1]</sup> In this sense, there has been growing interest in phosphorus-containing  $\pi$ -conjugated compounds and polymers.<sup>[2]</sup> Particularly, outstanding progress has been made in the field of phosphole-based functional materials over the last decade:<sup>[3]</sup> the applications to OLED emitters<sup>[4]</sup> and bioimaging probes<sup>[5]</sup> represent remarkable highlights. Yet, for bringing further flexibility and diversity to design principles for organophosphorus  $\pi$ -conjugated functional materials, novel promising P-containing building blocks and synthetic methodologies thereof should be explored.<sup>[6]</sup> In association with such synthetic challenges, the existing phosphorus-incorporated  $\pi$ -conjugated polymers have been limited to poly(phosphole)s,<sup>[7]</sup> poly(p-arylene/vinylene phosphane)s,<sup>[8]</sup> poly(p-phenylene phosphaalkene/diphosphene)s,<sup>[9]</sup> and poly(*p*-phenylenediethynylene phosphane)s.<sup>[10]</sup>

To tackle the challenges, we have recently developed new Pcontaining electron-acceptors, DPITOs (Figure 1a),<sup>[11a]</sup> and revisited related aromatic-fused diketophosphanyl compounds.[11b] In addition, the Baumgartner group has reported seven-membered diketophosphanyl compounds, DTDKPs (Figure 1a), as a unique building block for functional organophosphorus molecules.<sup>[12]</sup> Nevertheless, from the viewpoint of structural diversity of diketophosphanyl compounds, only 5-6-5,<sup>[11a]</sup> 5-7-5,<sup>[12]</sup> 6-7-6,<sup>[13b,d]</sup> 6-12-6,<sup>[13e]</sup> 5-6,<sup>[13a,b,c]</sup> and 6-6-6-fused<sup>[13d]</sup> ring systems have been reported to date. Moreover, diketophosphanyl-containing conjugated polymers are unknown.

Herein, we disclose a novel diketophosphanyl building block, thieno[3,4-c]phosphole-4,6-diones (TPHODOs, Figure 1b). A blueprint was drawn up by focusing on the struc-

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Figure 1. Diketophosphanyl-based functional molecules and building blocks.

ture of their N-surrogates, TPYRDOs (Figure 1 b).<sup>[14]</sup> The TPYRDO skeleton has been emerging as a promising electronacceptor (A) unit for constructing donor-acceptor (D-A) conjugated low-bandgap polymeric materials for photovoltaics,<sup>[15]</sup> due to its synthetic modulability, good electron-accepting ability, high planarity, and quinoidal character for effective extension of  $\pi$ -systems along the polymer backbone. Additionally, such low-bandgap materials that absorb and/or emit near-IR (NIR) light can find numerous applications like photodetectors and security information displays.<sup>[16]</sup> Based on this background, we envisioned that TPHODOs serve as a unique acceptor building block for assembling P-containing D-A  $\pi$ -conjugated systems spanning from small molecules to polymers, beyond the precedent nitrogen-based systems. For example, TPHODOcored D-A conjugated molecules and polymers can have lower bandgaps ( $E_{a}$ ) than those of the corresponding nitrogen surrogates, given that the (C–P) $\sigma^*$ - $\pi^*$  orbital coupling operates effectively. Moreover, the versatile reactivity of  $\sigma^3$ , $\lambda^3$ -P-centers<sup>[17]</sup> would allow for fine-tuning the optoelectronic properties of the polymers through post-polymerization modification.[7d, 10]

Initially, we established preparative methods for the simplest TPHODOs 1 and 2 (Scheme 1 a).<sup>[18]</sup> The condensation of S1 with  $[(Tipp)P(SiMe_3)_2]$  (Tipp = 2,4,6-triisopropylphenyl), which was generated in situ through deprotonation/silylation of (Tipp)PH<sub>2</sub>, afforded **1** in 44% yield (Scheme 1a). Importantly, yellowish compound 1 was stable enough to be isolated by column chromatography on silica gel, probably due to the presence of two electron-withdrawing carbonyl groups.[11] The structure of 1 was fully characterized by spectroscopic methods such as <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR ( $\delta$  = +7.54 ppm).<sup>[18]</sup> In a similar

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201602392.



#### CHEMISTRY A European Journal Communication



Scheme 1. a,b) Synthetic routes to 1-4; c) P-functionalization of 1, 3, and 4.

manner, 1,3-dibrominated TPHODO 2 was prepared in a moderate yield (Scheme 1 a). Through this method, a variety of analogous TPHODOs were prepared from S2 and  $[RP(SiMe_3)_2]$  (R = Cy (Cy-2), Ph (Ph-2), Mes (Mes-2; Mes=2,4,6-trimethylphenyl)).<sup>[18]</sup> As the result of screening of coupling conditions, the Pd-catalyzed Migita-Kosugi-Stille coupling, applying 2 as an acceptor and mono- and bithienyl tributylstannanes as donors, was found to be effective for assembling D-A-D compounds 3 and 4 in high yields (Scheme 1b). Notably, the presence of a sterically demanding group (Tipp) on the P-center was key to the successful cross-coupling: phosphorus compounds bearing a less-bulkier groups on the P-centers (Cy-2 and Ph-2) did not give coupled products, even though they were consumed (Table S1, Supporting Information). On the other hand, Mes-2 gave the corresponding doubly coupled product Mes-3 in a moderate yield.<sup>[18]</sup> The nitrogen surrogates TPYRDOs (N-1-N-4) were also prepared as reference compounds.<sup>[18]</sup> Most importantly, the developed  $\sigma^3$ ,  $\lambda^3$ -phosphorus compounds are functionalizable on the P-centers (Scheme 1 c). Treatment of 1 with [Au(tht)Cl] (tht = tetrahydrothiophene) provided  $\sigma^4$ -phosphorus complex 1-AuCl in 90% yield, whereas 4-AuCl was obtained from 4 in 82% yield (Scheme 1c). The coordination of Au to the P centers caused significant upfield shifts of <sup>31</sup>P NMR resonances ( $\Delta\delta$  (**1-AuCl**) = -2.50 ppm;  $\Delta\delta$  (**4-AuCl**) = -2.20 ppm). The oxidation of 3 and 4 with meta-chloroperoxybenzoic acid (mCPBA) gave the corresponding oxides 3-O and 4-O, respectively (Scheme 1c).<sup>[19]</sup>

The single crystals of **Mes-2**, **3** and **N-2** suitable for the X-ray crystallographic analysis were grown from  $CH_2Cl_2$ /hexane solutions.<sup>[20]</sup> It should be noted that this is the first report to elucidate the molecular geometry of 5–5-fused diketophosphanyl compounds (Figure 2). As expected, the P-centers of **Mes-2** and **3** adopt trigonal pyramidal structures (Figure 2a and c) that are deviated from the mean plane of the thiophene-carbonyls with distances of 0.49 and 0.67 Å, respectively. An intriguing feature about the packing structures of **Mes-2** involves

Figure 2. ORTEP drawings of a) Mes-2 and c,d) 3 (H atoms are omitted for clarity); dimeric pairs of b) Mes-2 and e) 3 (*i*Pr groups and H atoms are omitted for clarity).

the dimeric pairs that are apparently connected through a pair of self-complementary two-point halogen bonds (XBs)<sup>[22]</sup> (C-Br···O=C, Figure 2 b), as evidenced by the linearity (<C–Br···O= 172°) and the shorter distance [d(Br...O) = 3.08 Å] than the sum of van der Waals radii (3.37 Å).<sup>[23]</sup> The nitrogen surrogate of 2 (N-2) also adopts self-complementary XB motifs to form a 1Dsheet in the solid state (Figure S15a, Supporting Information). Since such self-complementary multipoint XB motifs are very rare in the literature,<sup>[24]</sup> but should serve as a mimic of hydrogen-bonding counterparts,<sup>[25]</sup> these findings would offer an opportunity for utilizing the 1,3-dibromo-TPHODO and related structures as fundamental motifs in crystal engineering. The terthiophene unit of 3 lies coplanar (Figure 2c) and perpendicular to the Tipp ring (Figure 2d). In both cases, the lengths of the endo- (1.85-1.87 Å) and exocyclic P-C bonds (ca. 1.82 Å) are almost the same as those of reported diketophosphanyl compounds.<sup>[11, 12a, 13e, 21]</sup> The terthiophene units of **3** are stacked in a face-to-face manner so that the two diketophosphanyl units point to opposite sides, with the interplane distance of 3.55 Å (Figure 2 e).

Figure 3 a illustrates the UV/Vis and PL spectra of 1, 3, 4, and 4-O, and the properties of TPHODOs are summarized in Table 1.<sup>[18]</sup> The CH<sub>2</sub>Cl<sub>2</sub> solution of 1 showed a strong absorption at around 250 nm that corresponds to a H—5→L transition, which was assigned by TDDFT calculation (Table S7, Supporting Information), and a weak n– $\pi^*$  absorption (H—1→L transition) at around 320 nm (Figure 3 a). As the  $\pi$ -system was extended, the peaks in the lower-energy regime (300–560 nm) assignable to  $\pi$ – $\pi^*$  (H→L) transitions significantly redshifted (1: 329 nm, 3: 400 nm, 4: 484 nm). In line with the increased overlap between the HOMOs and LUMOs (1 < 3 < 4, Figure S17, Supporting Information), the molar absorption coefficient ( $\varepsilon$ ) drastically increased in the same order. The absorptions in the higher

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Compd $\lambda_{abs} [nm]^{[a]} (\varepsilon [M^{-1} cm^{-1}]) \qquad \lambda_{em} [nm]^{[a]} (\Phi_{PL})$	$D^{(b)} = \sum_{onset} e^{-\alpha t} E_{1/2} [V vs. Fc/Fc^+]^{(c)} = E_{HOMO} E_{LUMO} [eV]$
1 329 (3,700) ND (-)	ND/-2.00 <sup>[d]</sup> -6.58 <sup>[f]</sup> /-3.10
1-AuCl 380 (450) ND (-)	0.99/-1.53 <sup>[d]</sup> -6.09/-3.57
<b>3</b> 400 (15,000) 492 (0.01)	ND/-1.84 -5.91 <sup>[f]</sup> /-3.26
<b>3-0</b> 448 (7,600) 561 (< 0.01)	ND/-1.42 -6.04 <sup>[f]</sup> /-3.68
<b>4</b> 484 (34,000) 573 (0.07)	0.12/-1.72 -5.22/-3.37
<b>4-0</b> 540 (21,000) 650 (0.02)	0.18/-1.37 -5.28/-3.73
<b>4-AuCl</b> 515 (10,000) 591 (0.01)	0.73/-1.44 <sup>[d]</sup> -5.83/-3.66

[a] Measured with  $CH_2CI_2$  solutions ( $10^{-5}$  m). [b] Determined with an integrating sphere. [c] Measured by CV using  $CH_2CI_2$  solutions ( $10^{-3}$  m) containing  $nBu_4N$ ·PF<sub>6</sub> as an electrolyte. [d] The onset potential. [e]  $E_{HOMO}$ =-(5.1 + <sup>ox</sup> $E_{onset}$ ) [eV];  $E_{LUMO}$ =-(5.1 + <sup>red</sup> $E_{1/2}$ ) [eV]. [f]  $E_{HOMO}$ =- $E_{LUMO}$ -1240/<sup>onset</sup> $\lambda_{abs}$  [eV].

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Figure 3. a) UV/Vis and PL spectra of 1, 3, 4, and 4-O ( $10^{-5}$  M CH<sub>2</sub>Cl<sub>2</sub> solutions); b) frontier orbitals and energy diagrams of 4, 4-O, and N-4 calculated by the DFT method.

energy regime (240–360 nm) were redshifted, and  $\varepsilon$  was decreased, in the order of 1, 3, and 4 (Figure 3a), which was probably caused by the change in the transitions from  $\pi$ - $\pi$ \* to mixed  $n-\pi^*$  and  $\pi-\pi^*$  character. Diketophosphanyl compounds 3 and 4 are emissive in solution under the UV irradiation (3: 492 nm, 4: 573 nm) with subnanosecond order lifetimes (Table S3, Supporting Information). Notably, the P-functionalization of 3 and 4 resulted in a significant redshift in both of the absorption (e.g., 4: 484 nm, 4-AuCl: 514 nm, 4-O: 540 nm) and the emission (e.g., 4: 573 nm, 4-AuCl: 591 nm, 4-O: 650 nm). To investigate the effects of the P-incorporation, the properties were compared with those of N-1, N-3, and N-**4**.<sup>[18]</sup> Taking **4** and **N-4** as an example, both of  $\lambda_{abs}$  and  $\lambda_{em}$  of **4** locate in the lower-energy region compared with those of the imide counterpart (**4**:  $\lambda_{abs} = 484$  nm,  $\lambda_{em} = 573$  nm; **N-4**:  $\lambda_{abs} =$ 450 nm,  $\lambda_{em}$  = 530 nm), indicating the validity of the P incorporation to narrow the HOMO-LUMO band gaps as well as to tune emission color to longer wavelength. Regarding quantum yields ( $\Phi_{\rm PL}$ ), phosphorus compounds showed lower  $\Phi_{\rm PL}$  than those of the corresponding nitrogen surrogates,<sup>[18]</sup> probably due to the existence of extra nonradiative decay channels, such as dynamic pyramidal inversion<sup>[11a]</sup> and internal conversion when compared with rigid and planar imide compounds.

CV revealed the energy profiles of the TPHODOs (Table 1 and Figure S7–S9, Supporting Information). Compared with the N-surrogates, the LUMO energies of 3 and 4 are lower than those of N-3 and N-4 by more than 0.1 eV, indicating the operation of  $\sigma^* - \pi^*$  electronic coupling in these phosphorous compounds. It is noted that the Au-complexation of 1 and 4 resulted in complex electrochemical profiles (Figure S8, Supporting Information), which made it difficult to precisely determine their redox potentials. Nevertheless, from the tentatively identified onset reductive potentials ( $^{red}E_{onset}$  –1.53 and –1.44 eV for 1-AuCl and 4-AuCl, respectively), the ELUMO of the gold complexes were lower than those of 1 and 4 (Table 1), probably due to the decreased electron densities of the diketophosphanyl rings through P-coordination to Au atoms. In contrast, P-oxidation (3-O and 4-O) gave clear CV profiles, and distinctive reversible reduction waves were observed (Figure S8b, Supporting Information) in the more positive potential regime when compared with 3 and 4 (Table 1).

TGA profiles of TPHODOs revealed their high stabilities for trivalent phosphorus compounds (Figure S10–S13, Supporting Information), probably because of the existence of two electron-withdrawing carbonyl groups. Such high thermostability would be a favorable feature for practical use as organic materials.

For further understanding the impact of P-incorporation and P-functionalization, theoretical calculations using the DFT method were performed (Figure 3 b).<sup>[18]</sup> When compared with **N-4**, the  $E_{HOMO}$  of **4** (-5.77 eV) is almost the same as that of **N-4** (-5.75 eV), while a significant stabilization of the  $E_{LUMO}$  was gained by more than 0.1 eV, in agreement with the results of CV experiments. This would be caused by the operation of  $\sigma^*$ - $\pi^*$  orbital coupling, which is supported by the largely developed LUMO orbitals around the P-center (Figure 3 b). Notably, the P-oxidation of **4** resulted in a drastic stabilization of the  $E_{LUMO}$  by 0.3 eV and a slight drop of  $E_{HOMO}$ , leading to the narrower HOMO-LUMO band gap (2.79 eV) than those of **4** (3.00 eV) and **N-4** (3.09 eV). This is again consistent with the CV experiments and the redshift trend in absorption/PL spectra in the order of **N-4** < **4** < **4-O**.

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To demonstrate the versatility of the TPHODO building block **2**, P-containing conjugated polymers **P1** and **P2**, along with the reference **N-P1**, were synthesized through a Pd-catalyzed cross-coupling polymerization (Scheme 2).<sup>[18]</sup> The presence of the TPHODO unit was confirmed by <sup>13</sup>C and <sup>31</sup>P NMR (e.g., the carbonyl <sup>13</sup>C resonance of **P1**:  $\delta$  = 204.4 ppm, the <sup>31</sup>P resonances were found to range from  $\delta$  = +8.42 to +9.25 ppm with the largest peak at  $\delta$  = 9.24 ppm).<sup>[18]</sup>

Properties of synthesized polymers are summarized in Table 2. The CH<sub>2</sub>Cl<sub>2</sub> solutions of **P1** and **P2** absorb almost all the visible light as well as NIR light up to 800 nm (Figure 4a) and are emissive in the NIR region (**P1**: 753 nm, **P2**: 712 nm) under UV irradiation (Figure 4b). When compared with the nitrogen analogue of **P1** (**N-P1**), the optical bandgaps (<sup>opt</sup>*E*<sub>g</sub>) of **P1** (1.53 eV) and **P2** (1.47 eV) were found to be much narrower than that of **N-P1** (1.63 eV), in line with the similar trend with small molecules. The electrochemical bandgap (<sup>elc</sup>*E*<sub>g</sub>) reasonably agreed with <sup>opt</sup>*E*<sub>g</sub>. Nota-

bly, as **P1** was titrated with an aliquot of [Au(tht)Cl] in  $CH_2CI_{2'}^{[18]}$  the absorbance in the NIR region from 650 to 800 nm gradually increased, while the absorption in the region



Scheme 2. Synthesis of low-bandgap polymers a) P1 and P2; b) N-P1.

of 500–650 nm decreased, as a function of the amount of Au added (Figure 4c). After the titration, the <sup>31</sup>P resonances of **P1** were shifted to the upper-filed (i.e., the main resonance

Table 2. Properties of polymers.										
Polymer	$\lambda_{\mathrm{abs}}~[\mathrm{nm}]^{\mathrm{[a]}}$	$\lambda_{ m em}~[ m nm]^{[a]}$	$\varPhi_{\rm PL}{}^{\rm [a,b]}$	$\lambda_{\text{onset}} \text{ [nm]}^{[c]}$	$^{opt}E_{g} [eV]^{[d]}$	$^{ox}E_{onset}$ [V vs. Fc/Fc <sup>+</sup> ] <sup>[e]</sup>	$^{red}E_{onset}$ [V vs. Fc/Fc+] <sup>[e]</sup>	$E_{\rm HOMO}  [\rm eV]^{[f]}$	E <sub>LUMO</sub> [eV] <sup>[f]</sup>	$^{elc}E_{g}$ [eV] <sup>[g]</sup>
P1	624	712	0.17	810	1.53	0.34	-1.27	-5.44	-3.83	1.61
P2	681	753	0.14	840	1.47	0.34	-1.14	-5.44	-3.96	1.48
N-P1	578	673	0.23	759	1.63	0.52	-1.30	-5.62	-3.80	1.82

[a] Measured with CH<sub>2</sub>Cl<sub>2</sub> solutions (0.5 wt%). [b] Determined with an integrating sphere. [c] Measured with thin-films on a quartz plate. [d]  $^{opt}E_g = (1240/\lambda_{onset})$  [eV]. [e] Determined by CV using thin-films deposited on a Pt working electrode. [f]  $E_{HOMO} = -(5.1 + ^{ox}E_{onset})$  [eV];  $E_{LUMO} = -(5.1 + ^{red}E_{onset})$  [eV]. [f]  $^{elc}E_g = {}^{ox}E_{onset} - {}^{red}E_{onset}$  [eV].



Figure 4. a) Absorption and b) PL spectra of CH<sub>2</sub>Cl<sub>2</sub> solutions (0.5 wt %) of the polymers. c) Gradual changes in UV spectra of P1 as a function of the amounts of [Au(tht)Cl] added.

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moved from  $\delta = +9.24$  to +7.98 ppm), which is consistent with the behavior of 1 and 4 in Au-complexation. Since almost no change in UV spectra was observed in the control experiment using N-P1 instead of P1 (Figure S6c, Supporting Information), the spectra change in the case of P1 would have been caused as a result of the interaction between P and Au moiety. In conjunction with the existence of isosbestic points (e.g., at around 660 nm), it is speculated that this spectral change corresponds to the coordination of the P-centers to the Au centers in a 1:1 manner. Although this preliminary phenomenon awaits further investigations, the bottom line is that the post-polymerization functionalization of P1 successfully allowed for the bandgap control ranging from 1.72 to 1.51 eV only by regulating the amount of Au to be added.

In summary, we have developed novel phosphorus-containing building blocks, TPHODOs. The utility of the building block was demonstrated by creating new D–A–D functional molecules and low-bandgap conjugated polymers. Moreover, the bandgap control through post-polymerization modification of the polymer has been achieved. Further studies focused on the utilization of developed polymers as functional materials are ongoing in our laboratory.

#### Acknowledgements

This research was supported by a Grant-in-Aid for Scientific Research on Innovative Areas " $\pi$ -System Figuration: Control of Electron and Structural Dynamism for Innovative Functions" (KAKENHI Grant Number 15H00997) from the Ministry of Education, Culture, Science and Technology, Japan (to Y.T.) and by the Shorai Foundation for Science and Technology (to Y.T.). The authors gratefully acknowledge the experimental assistance of Profs. A. Saeki, Y. Yakiyama, and H. Sakurai (Osaka University).

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- [19] Although the Au-complexation of 3 also seemingly proceeded, the difficulty in isolation of the resulting Au complex did not lead to the characterization. Furthermore, the oxidation of 1 did not proceed under the similar conditions using *m*CPBA and H<sub>2</sub>O<sub>2</sub>. Other P-functionalizations of 1, 3, and 4 with S<sub>8</sub>, Pd, and W complexes failed to give characterizable products.
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Received: May 19, 2016 Published online on ■■ ■, 0000

#### Chem. Eur. J. 2016, 22, 1–6 www.c

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# COMMUNICATION

#### Photophysics

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#### 

Thieno[3,4-c]phosphole-4,6-dione: A Versatile Building Block for Phosphorus-Containing Functional π-Conjugated Systems



small molecules to low-band gap polymers!

**Donor–acceptor systems**: A novel class of phosphorus-containing conjugated building blocks, thieno[3,4-*c*]phosphole-4,6-diones (TPHODOs), has been developed (see scheme). Utilizing the building block, phosphorus-containing D-A-D-conjugated compounds and lowbandgap conjugated polymers based on donor-acceptor (D-A) architecture have been synthesized.