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COMMUNICATION

A biphenyl containing two electron-donating and two accepting moieties: a rigid and small donor-acceptor-donor ladder system

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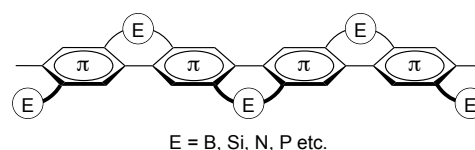
Ladder π-conjugated materials and also push-pull systems belong to important classes of compounds for the development of organic electronic devices. In this communication, a novel π-conjugated material that unifies properties of both of these classes is presented. The material comprises a rigid biphenyl framework which bears two bridging electron-accepting phosphine oxide moieties as well as two electron-donating amino groups. Structure and photophysical properties of this compound are discussed and compared with those of a related system lacking the second P-moiety.

The development of functional materials has received great attention in the past decades. The constantly growing requirements of electronic devices such as organic light-emitting diodes (OLEDs),[1] field-effect transistors (FETs)[2] and photovoltaic cells[3] concerning performance, size and weight ask for novel types of organic π-systems. Along these lines, various classes of compounds have been developed, for example π-conjugated oligomers or polymers,[4] polycyclic aromatic hydrocarbons[5] or ladder-type π-electron systems.[6] Incorporation of main group elements into the π-skeleton of these materials as a bridging unit has been shown to be a valuable strategy for the fine-tuning of functions and properties (Figure 1a).[6b] A key aspect is that effective π-conjugation comes along with the rigidity and flatness of the given structure. In addition, a "dopant" element, in particular phosphorus, allows for variation of the physical properties by simple chemical modification, such as complexation with Lewis acids or metals, and alkylation towards phosphonium salts.[7] Oxidation to phosphine oxides or sulfides also offers ready access to electron-accepting π-conjugated materials. Beyond incorporating main group elements into an organic π-conjugated framework, the combination of strong electron-donating groups with highly electron-accepting moieties thereby forming so called push-pull chromophores leads to promising π-materials (Figure 1b).[3c] Herein, we present the synthesis and photophysical properties of a biphenyl system featuring electron-accepting bridging units in a ladder-type system that further contains electron-donating substituents. This compound can be considered as one of the smallest known ladder-type donor-acceptor-donor π-systems (Figure 1c).

Radical phosphanylation has recently been shown to be a highly useful and practical method for the synthesis of arylphosphanes.[8] For example, we successfully applied radical phosphanylation to the
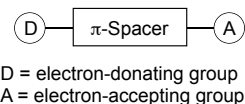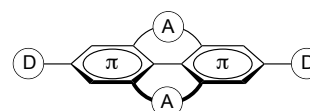

Fig 1 a) ladder-type organic π-conjugated materials with main group element bridges and b) a ladder-type donor-acceptor-donor system studied in this work.

preparation of bis(phosphoryl)-bridged biphenyls.[9] Similarly, Liu and coworkers used this method to access bisphosphole-bridged ladder oligophenylenes.[10,11] Encouraged by these results, we decided to use this reaction as a key step for the synthesis of conjugated polycyclic π-systems bearing phospholes as rigidifying electron-accepting entities along with nitrogen substituents as electron-donating moieties,[12] representing small and rigid ladder-type donor-acceptor-donor biphenyls.

Readily accessible *N,N*-dibenzyl-3,5-dibromoaniline (**1**) was first homocoupled with FeCl₃ to benzidine derivative **2** (Scheme 1).[13] Biphenyl **2** was characterized by X-ray analysis revealing, as expected, that the phenyl planes of the biphenyl core show a torsion

angle of around 90° (see Supporting Information). Radical phosphanylation of **2** with PhP(SnMe₃)₂ initiated by 1,1′-azobis(cyclohexanecarbonitrile) (V-40) and subsequent oxidation with H₂O₂ afforded the desired *trans*-bis(phenylphosphoryl)-bridged benzidine **3a** as a single diastereoisomer. As this *P*-phenylated derivative has only limited solubility to CH₂Cl₂, we also tried to synthesize a *P*-alkylated derivative. Using *n*-OctylP(SnMe₃)₂ as a new phosphorus source, we obtained an octyl-substituted derivative **3b**, which has improved solubility to various solvents even including toluene.
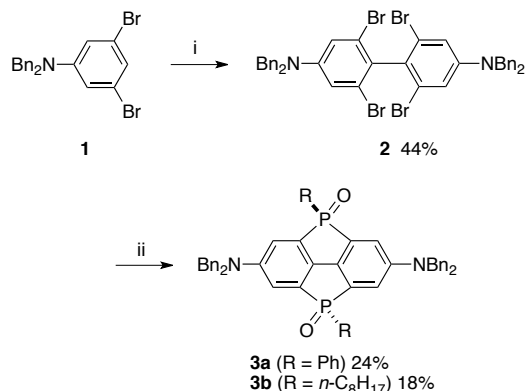
Scheme 1 Synthesis of donor-acceptor-donor system **3**; i: FeCl₃·6 H₂O, PhCH₃, 85 °C, 24 h, ii: a) PhP(SnMe₃)₂ or *n*-OctylP(SnMe₃)₂, V-40, PhCF₃, 125 °C, 72 h; b) H₂O₂, CH₂Cl₂, rt, 3 h.

Successful preparation of **3a** and **3b** demonstrates the great potential of this multiple phosphanylation process, which occurs *via* sequential fourfold homolytic substitution at phosphorus by aryl radicals. Notably, the produced four ring-fused P-heterocyclic compounds build up high ring strain within the π-system, according to the X-ray crystal structural analysis of **3a** (Figure 2). A characteristic feature of this remarkable class of triarylphosphine oxides is the elongated endocyclic C–P bond (1.840(3)–1.841(3) Å) which belongs to the longest among the reported examples.[9] A further indication of a strained π-system is the length of the central C–C bond (1.437(6) Å). Compared to precursor **2** (1.482(5) Å), this C–C bond is significantly shortened in order to overcome the induced ring strain that is caused by the two annulated phosphine oxide moieties. The arene entities in the biphenyl core are coplanar (torsion angle (C1C4C4*C1*) = 0°), suggesting effective π-conjugation. Importantly, both of the terminal amino groups adopt a planar geometry, in which the lone pairs of the nitrogen atoms are in perfect conjugation with the π-system. Similar characteristic features are also observed for the crystal structure of the octyl-substituted **3b** (Figure S4 in the ESI).
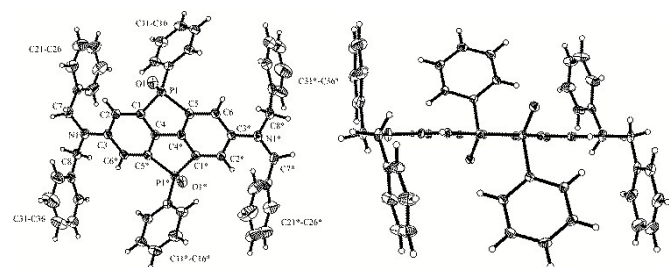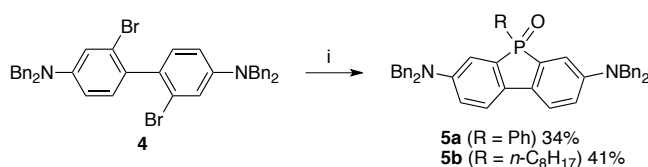

Fig 2 X-ray crystal structure of **3a**. Top view (left) and side view (right). Thermal ellipsoids are shown with 30% (left) and 15% (right) probability.

Scheme 2 Phosphorylation to benzidine **5**; i: a) PhP(SnMe₃)₂ or *n*-OctylP(SnMe₃)₂, V-40, PhCF₃, 125 °C, 48 h; b) H₂O₂, CH₂Cl₂, rt, 3 h.

In order to elucidate the influence of the two phosphole moieties on the structure and properties of **3**, we also prepared the corresponding mono(phosphoryl)-bridged benzidines **5a** and **5b**, which represent less strained congeners of **3** (Scheme 2). These compounds were obtained by using the same chemistry starting with dibromide **4**.[14] The structure of **5a** was confirmed by X-ray structural analysis, which revealed that the endocyclic C–P bonds in **5a** are, as compared to those of benzidine **3a**, much shorter (C2–P1 = 1.792(12) Å; C8–P1 = 1.803(11) Å, see Supporting Information). Again the two N-lone pairs are in conjugation with the biphenyl π-system. However, due to the low quality of the single crystals, the exact bond lengths are afflicted with a marginal error in the case of phosphoryl-bridged benzidine **5a** (see the ESI).

Next, we studied the effect of the substitution pattern of the biphenyl core on the molecular orbital energies and performed calculations at the B3LYP/6-31G(d) level of theory.[15] For better comparison we also included compound **6** which was previously prepared in our laboratories[9] into these studies. It was known that the introduction of electron-withdrawing phosphoryl groups
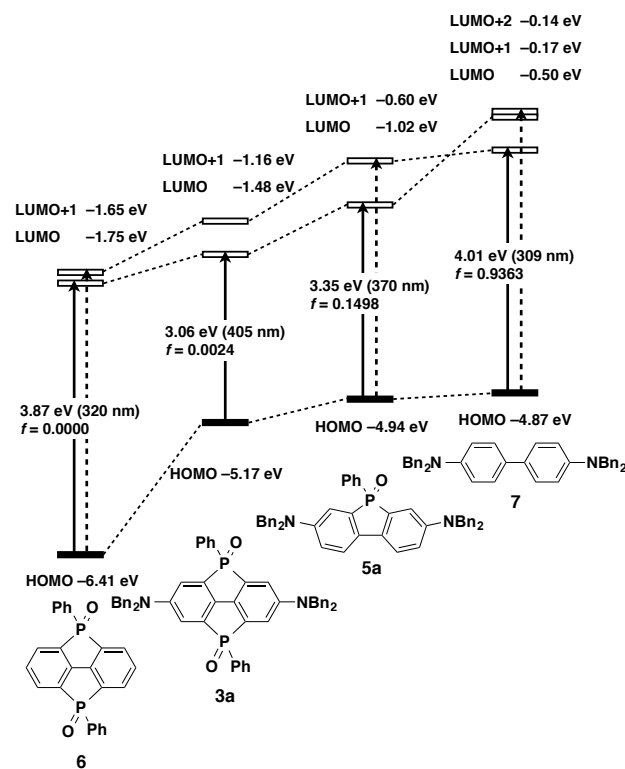
Fig 3 Relative molecular orbital energies of bisphosphole **6** and donor-acceptor-donor systems **3** and **5** (B3LYP/6-31G(d) level) and the S₀–S₁ transition energies estimated by the TD DFT calculations at the same level of theory. The results of bis(dibenzylamino)biphenyl **7** fixed in a coplanar geometry are also shown for comparison. The vertical solid and dotted arrows represent the major and minor components for each transition.

considerably stabilizes the energy of the LUMO of bisphosphole **6** compared to the parent biphenyl.[9] On the other hand, two electron-donating amino groups increase the electron density of the π-system and thus the orbital energies of bis(phosphoryl)-bridged benzidine **3a** (Figure 3). The fact that the LUMO energy is less affected than the HOMO by these substituents results in a significantly narrower HOMO–LUMO gap of $\Delta E = 3.69$ eV for **3a** as compared to 4.84 eV for **6**. The second phosphine oxide moiety is essential to gain the narrow HOMO–LUMO gap, as one can see by comparison of the calculated energies for the mono-phosphorylated congener **5a**, which shows a HOMO–LUMO gap of $\Delta E = 3.92$ eV.

The photophysical properties of both mono- and bis-phospholes **3** and **5** were evaluated next and compared with the data reported for **6**. The absorption as well as emission spectra are depicted in Figure 4 and the data are summarized in Table 1. The UV/Vis absorption spectra of bis(phenylphosphoryl)-bridged benzidine **3a** in CH_2Cl_2 shows an absorption band with the maximum wavelength of $\lambda_{abs} = 464$ nm with rather small absorption coefficient of $\varepsilon = 870$. Notably, compound **3a** exhibits an orange emission with the maximum wavelength of $\lambda_{em} = 594$ nm in the fluorescence spectrum in CH_2Cl_2. Compared to the parent bis(phosphoryl)-bridged biphenyl **6** ($\lambda_{abs} = 347$ nm, $\lambda_{em} = 387$ nm) or mono(phosphoryl)-bridged benzidine **5a** ($\lambda_{abs} = 431$ nm and $\lambda_{em} = 505$ nm),[9] both the absorption and emission wavelengths of **3a** are significantly red-shifted. These differences demonstrate the significant impacts of the combination of two electron-donating amino groups and two electron-accepting phosphoryl moieties on the photophysical properties.

Table 1: Photophysical data for the phospholes.[a]

Compound	UV/Vis Absorption		Emission
	λ_{abs} [nm][b]	ε [×10³]	λ_{em} [nm][c]
3a	464	0.87	594
3b	452	1.03	569
5a	431	3.08	505
5b	415	3.47	488
6[d]	347	0.37	387

[a] In CH_2Cl_2. [b] Only the absorption maxima at the longest wavelength are shown. [c] Excited at the absorption maximum wavelength. [d] Reference 9.
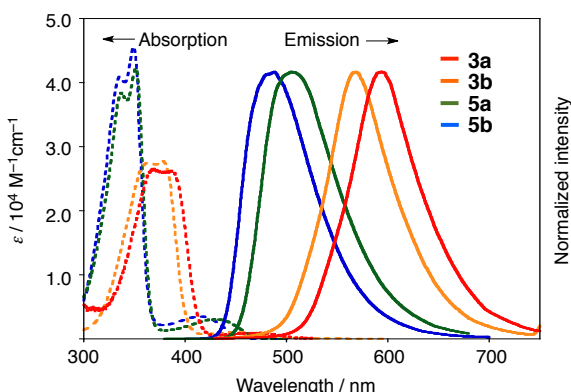

Fig 4 Absorption (dotted line) and emission (solid line) spectra of **3** and **5**.

To gain insights into the effect of the donor-acceptor-donor skeleton in **3** on the properties, the solvent effects were investigated by employing more soluble octyl-substituted derivative **3b**, which has slightly shorter absorption and emission maximum wavelengths compared to **3a**. Interestingly, unlike the ordinary donor-acceptor-donor systems, **3b** did not show any noticeable solvatochromism both in the absorption and fluorescence spectra (λ_{abs} and λ_{em}: 446 and 556 nm in toluene; 453 and 572 nm in $CHCl_3$; 452 and 569 nm in CH_2Cl_2; 442 and 565 nm in acetone, respectively). This result implies no significant intramolecular charge transfer (ICT) character in the excited state for this compound. Time dependent (TD) DFT calculation at the B3LYP/6-31G(d) level indeed showed that the S_0–S_1 transition in **3** is attributable to not the ICT transition, but the π–π* transition from HOMO to LUMO, both of which delocalize over the biphenyl skeleton. This transition is, however, essentially symmetrically forbidden, in sharp contrast to the symmetrically allowed transition for the parent benzidine derivative **7** without the phosphoryl bridges (Figure 3). This difference results from the switching of the orbital symmetry of the LUMO and LUMO+1 between **7** and the phosphoryl bridged derivatives **3** and **5**. This is one of notable impacts of the incorporation of the electron-withdrawing phosphoryl groups. It is also noted that, despite the no ICT character in the excited state, the bisphospholes **3** have significantly large Stokes shift around 4600 cm⁻¹, which are much larger than those of **5** (ca. 3600 cm⁻¹). This difference is responsible for the significantly red-shifted fluorescence for **3** and represents unique character of the present small donor-acceptor-donor system.

Whereas the monophosphole derivative **5a** have a high fluorescent quantum yield of $\Phi_F = 0.67$ in CH_2Cl_2, that of **3a** is low of $\Phi_F = 0.03$. This difference is largely due to the longer-wavelength emission as well as the forbidden character of the S_0–S_1 transition for **3**, and thereby suppressed radiative decay process from the excited state.

In summary, we have presented the synthesis of phosphoryl-bridged benzidines by using radical phosphanylation and also evaluated their photophysical properties. Calculation of the molecular orbital energies showed narrow HOMO–LUMO gaps of 3.69 eV and 3.92 eV for benzidines **3** and **5**, respectively. Notably, these π-systems can be formally regarded as one of the smallest donor-acceptor-donor systems bearing two electron-donating and two electron-withdrawing moieties within a biphenyl core. Unlike the ordinary donor-acceptor-donor systems, however, these π-systems have no significant intramolecular charge transfer character in the excited state and thereby do not show any noticeable fluorescent solvatochromism. Nevertheless, these compounds still exhibited a large bathochromic shift of the emission wavelength and showed orange fluorescence. This work highlights the value of organic π-materials possessing a phosphoryl-bridged arene backbone conjoined with electron-donating substituents and their great potential to be applied as building blocks in functional materials.

Notes and references

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Electronic Supplementary Information (ESI) available: Experimental procedures, spectroscopic and crystallographic data as well as computational details are included in the SI. See DOI: 10.1039/c000000x/

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14 An attempt to introduce the phosphine moiety using halogen-metal exchange and subsequent trapping with PhPCl$_2$ failed.

15 For detailed information see Supporting Information.