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Phosphorous Heterocycles

2,2′-Biphospholes: Building Blocks for Tuning the HOMO–LUMO Gap of π-Systems Using Covalent Bonding and Metal Coordination**

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Organic π-conjugated systems are useful lightweight semiconducting materials for electronics.[1] The control of their HOMO–LUMO energy gap (E_g) is one of the key issues in the optimization of these materials for applications (organic light-emitting devices (OLEDs), organic field-effect transistors (OFETs), photovoltaic cells, etc.).[2] The E_g of an isolated conjugated system (**A**; Figure 1) is a function of several structural factors including the bond-length alternation (E_{BLA}), aromatic character of the building blocks (E_{res}), electronic nature of the lateral substituents (E_{sub}), and the torsion angle between consecutive subunits (E_θ) (Figure 1).[2]

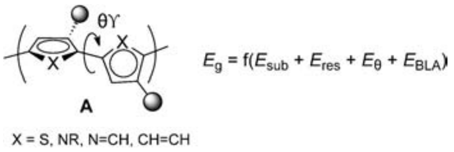

Figure 1. Structural factors determining the band gap of π-conjugated systems.

Among all these structural factors, only the torsion angle θ can potentially be varied in a continuous way to allow progressive switching from a highly delocalized low-gap system ($\theta = 0°$) to a non-delocalized high-gap system ($\theta = 90°$). However, this structural parameter is probably the most difficult factor to tune experimentally. In fact, the torsion angle can be fixed to 0° (fully planar systems) by rigidification through either the introduction of a covalent bond between the elemental building blocks (ladder-type molecules) or by metal coordination (for example 2,2′-bipyridines chelated by metal ions).[3] However, to date no general strategy that allows tuning of this torsion angle over a large range is known.

Herein, we show that exploiting the properties of the 2,2′-biphosphole unit **B** (modification of the substituents on P, or metal coordination; Figure 2)[4–6] allows a unique combined covalent/metal coordination approach for an on-demand tuning of the torsion angle θ between the two conjugated P heteroles. This simple and straightforward molecular engineering, which is not possible with other π-building blocks (2,2′-bipyridine, 2,2′-bithiophene, 2,2′-bipyrrole, 2,2′-bisilole, etc.), allows an unprecedented fine control of the energy gap, E_g, of the π-systems **A** (Figure 1) through two orthogonal approaches. Lastly, the impact of this tuning for optoelectronic applications is demonstrated with the use of 2,2′-biphosphole-based small molecules as emitting materials for OLEDs, including white organic light-emitting devices (WOLEDs).

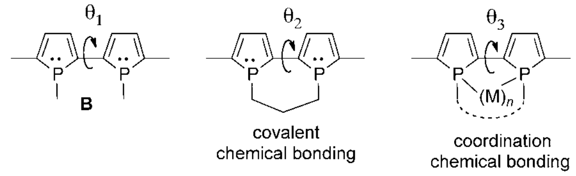

Figure 2. Covalent and metal coordination approaches to tune the torsion angles (θ) within the 2,2′-biphosphole building blocks.

The target 2,2′-biphosphole oligomers **2a–c** and **3b**,**c** (Scheme 1) were prepared from 1-aryl-3,4-dimethylphospholes **1a–c** using a synthetic strategy discovered by Mathey et al.,[5] and then later developed by Gouygou et al. for P-bridged derivatives.[6] The newly prepared compounds **2b** and **3b**,**c** were isolated in approximately 50% overall yield. The ^{31}P NMR spectroscopy shows that they exist as a mixture of stereoisomers, as already observed for related biphosphole

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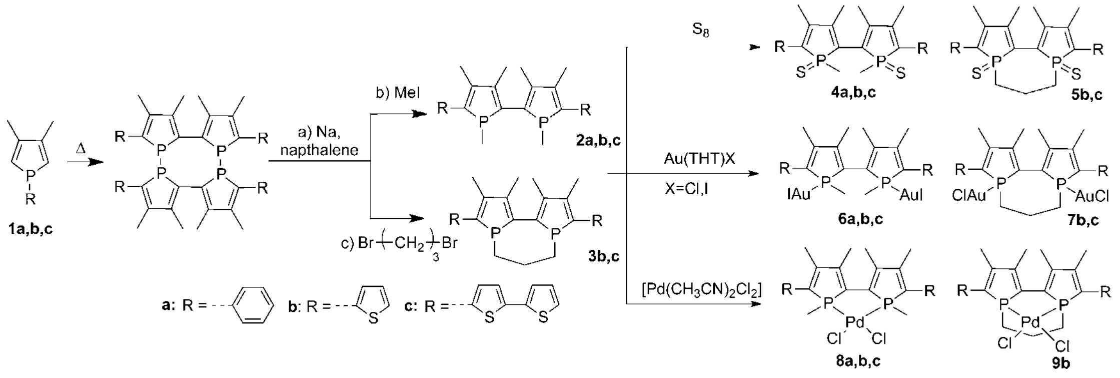

Scheme 1. Synthesis of the two series of 2,2′-biphospholes containing π-conjugated systems. THT = tetrahydrothiophene. Experimental conditions are given in the Supporting Information.

derivatives.[5,6] This synthetic approach allows the preparation of two series of biphosphole derivatives; one in which the two P rings are free to rotate about the inter-ring C–C bond (**2a**–**c**, Scheme 1), and one in which the two P rings have a restricted rotation because of their covalent bonding by a C_3 chain (**3b**–**c**, Scheme 1). These compounds were first transformed into the corresponding dithioxophospholes **4a**–**c**/**5b**,**c** (Scheme 1) to obtain air-stable and easy to handle derivatives. The sulfurization process is not diastereoselective but the major diastereoisomer was isolated by flash chromatography (ca. 60% yield). They were characterized by high-resolution mass spectrometry, elemental analysis, and multinuclear NMR spectroscopy.

Biphospholes exhibit a rich coordination chemistry, acting either as 1κ*P*,2κ*P* donors or as P,P-chelates.[4–6] We exploited this property, which is unique for π-conjugated ligands, to rigidify the biphosphole moiety using the coordination chemistry of different metal centers. Firstly, the novel Au^I complexes **6a**–**c** and **7b**,**c**, in which the two P centers act independently as two terminal donors, were prepared (Scheme 1). We expected that depending on the biphosphole series (free or restricted rotation), establishment of intramolecular Au^I–Au^I interactions[7] could offer a way to lock the torsion angle between the phosphorous heterocycles (Figure 2). Secondly, the Pd^{II} complexes **8a**-**c** and **9b**, in which the biphosphole unit acts as a bidentate donor, were synthesized (Scheme 1). It was also expected that, depending on the biphosphole series, different torsion angles could be obtained since the P donor can adopt a distorted geometry as a result of the high s character of its lone pair of electrons.[4] Note that all the Au^I and Pd^{II} complexes exhibit a single $^{31}P\{^1H\}$ NMR resonance, thus showing that the coordination processes are highly diastereoselective.[5,6] The newly prepared complexes were fully characterized by high-resolution mass spectrometry and elemental analysis. Their multinuclear NMR spectroscopy data compare well with those of related phosphole complexes[4–6,8] and support the proposed structures.

To evaluate the impact of this molecular engineering on the HOMO–LUMO gap of the corresponding π systems, the optical properties of all derivatives were investigated. All derivatives display an intense absorption band in the visible part of the absorption spectrum that is assigned to π–π* transitions of the extended π-conjugated system.[8] Three important trends are noteworthy. Firstly, as observed for the corresponding monophosphole-based π-conjugated systems,[8a–c] a noticeable red-shift of the absorption maximum (λ_{max}) is observed upon replacing the phenyl groups of **2a** by either 2-thienyl rings (**2b**; $\Delta\lambda_{max} = 22$ nm) or 5-(2,2′-bithienyl) substituents (**2c**; $\Delta\lambda_{max} = 61$ nm; see Table S1 in the Supporting Information). Secondly, the oxidation with elemental sulphur of the λ^3,σ^3-biphosphole units to give compounds **4** (Scheme 1) results in a blue-shift of the λ_{max} ($\Delta\lambda_{max} \approx 16$–20 nm, Table S1). In the solid state, this effect is less pronounced and the λ^3,σ^3-biphosphole and λ^4,σ^4-thioxobiphosphole derivatives exhibit similar absorption spectra. Overall, this behavior is very surprising since, in the case of all monophosphole-based π-conjugated systems, the reverse trend is observed (i.e. a red-shift of ca. 20 nm upon sulfurization of the P atom both in solution and solid state).[8,3e,f] Thirdly, the 2,2′-biphosphole/Au^I complexes **6a**–**c** (Scheme 1) display red-shifted UV/vis spectra ($\Delta\lambda_{max} \approx 10$–40 nm), and therefore smaller HOMO–LUMO gaps, than the corresponding thioxo derivatives **4a**–**c.** This result is unexpected, because for all π systems based on monophospholes known to date,[8,3ef] these two types of phosphole derivatives (Au^I complexes and thioxo derivatives) exhibit similar optical HOMO–LUMO gaps. These last two features demonstrate that phosphole and biphosphole building blocks behave very differently in the molecular engineering of π-conjugated systems, and are therefore a distinct series of building blocks.

The origin of these different behaviors of the biphosphole building blocks (electronic/steric) is not straightforward,[9] and to gain insight into these intriguing observations the solid-state structures of the thioxo derivatives **4a**–**c** and Au^I complexes **6a**–**c** were investigated. These X-ray diffraction studies show that in all cases racemic mixtures are obtained. Considering the mean plane between the two phosphole rings in **4b**, one can consider the sulfur atoms to occupy "axial" positions and the P-methyl substituents "equatorial" positions (Figure 3). The fact that the two P rings are free to rotate about the inter-ring C–C bond within the thiooxobiphosphole units is clearly shown by the different torsion angles between the two central P rings (**4a**: 81.0°; **4b**: 82.1°; **4c**: 51.0°). These

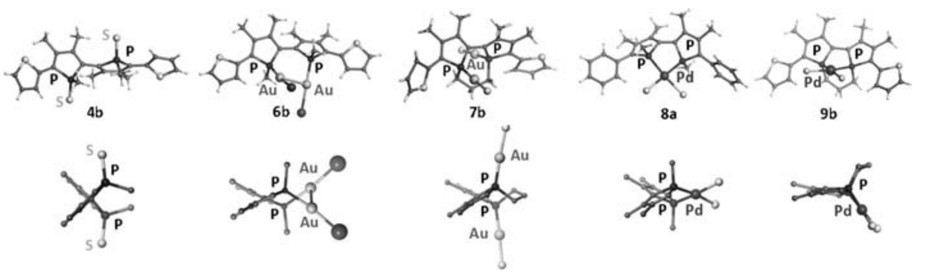

Figure 3. Views of the X-ray crystal structures of a 2,2′-biphosphole derivative series (see the Supporting Information for the other series).[11]

torsion angles are very high because of the tetrasubstituted P atoms which impose a twisted conformation to minimize steric congestion. These twisted conformations probably also exist in solution because of an additional steric repulsion of the methyl groups at the 3,4-positions of the P rings (**4b**, Figure 3). This structural feature can account for the rather high HOMO–LUMO gap of the thiooxobiphosphole derivatives **4a**–**c**. Complexes **6a**–**c** are also isolated as a racemic mixture, but the P-methyl substituents now occupy the axial positions (**6b**, Figure 3). This conformation, which contrasts to that of the thiooxophosphole derivative **4b** is due to the fact that two coordinated Au^{I} ions are engaged in aurophilic interactions[7] (**6a**: 2.9889(2) Å**,** **6b**: 3.050(4) Å; **6c**: 3.077(3) Å). This metallophilic interaction results in the formation of a $C_2P_2Au_2$ six-membered rings, which display a highly distorted chair conformation as a result of the long Au–Au distance and the presence of bulky methyl substituents (Figure 3). It is very likely that these six-membered rings exist in solution since 1) the energy associated with aurophilic interaction is about 10 kcal mol^{-1},[7] and 2) this conformation minimizes the steric repulsion between the ring substituents. Therefore, the metallophilic interactions lock the 2,2′-diphosphole subunits in place and the torsion angles between the two P rings are now fixed (**6a**: 51.3°, **6b**: 55.0°; **6c**: 54.2°). These torsion angles are lower than those recorded for their thioxophosphole analogues and can explain why these two series of derivatives exhibit different HOMO–LUMO gaps. This use of metal coordination to control the torsion angle of conjugated building blocks through metallophilic interactions nicely illustrates the impact of the biphosphole moiety for the molecular engineering of π-conjugated systems.

To further tune the torsion angle between the two central P rings of the biphosphole subunit, its bidentate behavior towards a Pd^{II} metal ion was exploited (Scheme 1, **8a**–**c**). The X-ray diffraction study of the complex **8a** reveals a square-planar metal center as part of a five-membered ring (Figure 3). Note that here the racemic mixture is also obtained and, as a result of the chelating behavior of the biphosphole fragment, the methyl groups occupy the axial positions. The formation of the five-membered ring upon coordination on the Pd^{II} ion imposes a large torsion angle within the biphosphole unit (87.7°). Furthermore, the phospholes rings are bent with respect to each other to help the phosphorus atoms to accommodate the square-planar coordination sphere of the Pd^{II} center (see Figure S2 in the Supporting Information). Interestingly, in accordance with the high torsion angle within the biphosphole unit, the π–π* transitions observed in the UV/Vis spectra of the Pd^{II} complexes **8a**–**c** are considerably blue-shifted compared to those of the Au^{I} complexes **6a**–**c** (for example: $\Delta\lambda_{\max} =$ 95 nm for **6c** versus **8c**; see Table S1 in the Supporting Informtion). These results clearly show how it is possible to fully exploit the biphosphole coordination chemistry to control their torsion angle using transition-metal atoms with specific properties, and to impact the HOMO–LUMO gap of the corresponding π-conjugated systems.

The versatility of this approach can be additionally extended to using 2,2′-biphosphole building blocks with a restricted rotational ability that results from a C_3 alkyl chain that is covalently bonded to the P atoms (derivatives **5**, **7**, and **9**; Scheme 1). Replacing the methyl substituent on P with the bridging C_3 alkyl chain has almost no influence on the UV/vis spectra of the corresponding π-conjugated systems that incorporate either the σ^3-biphosphole or σ^4-thioxobiphosphole building blocks (see Table S1 in the Supporting Information). Indeed, the solid-state structure of the dithioxophosphole derivative **6c** reveals a torsion angle of 67° between the two P rings, a value that is within the range of those recorded for the nonbridged compounds **4a**–**c.** These data show that the C_3 chain does not lock the biphosphole unit with a precise torsion angle and that a certain rotation about the inter-ring C–C is possible. In contrast to what was observed within the P–CH_3 series, the Au^{I} complexes **7b**,**c** exhibit absorption maxima that are similar to the corresponding dithioxophospholes **5b**,**c** (see Table S1 in the Supporting Information). The origin of this difference in behavior between the bridged and nonbridged series (Scheme 1) was rationalized by considering the solid-state crystal structure of complex **7b**. In this racemic mixture, which contains the bridging C_3 chain, the two Au^{I} ions occupy the axial positions and therefore cannot be engaged in aurophilic interactions (Figure 3). The torsion angle between the two P rings (64.9°) is controlled by the C_3 chain only and the P rings are not locked. As a consequence, the HOMO–LUMO gaps of these Au^{I} complexes **7b**,**c** are similar to those of the thioxobiphospholes **5b**,**c**, as observed for monophosphole-based π-conjugated systems. Indeed, the presence or absence of a covalent C_3 bridge between the P rings allows to change the relative position of the Au^{I} metal ions in the resulting complexes in order to control the torsion angle within the biphospholes. The trick to obtaining a biphosphole unit doubly locked through both covalent bonding and metal coordination, was to prepare the Pd^{II} complex **9b** using the precursor **3b** (Scheme 1). Indeed, the X-ray diffraction study of **9b** revealed a torsion angle of 25.8°, by far the smallest value observed within the biphosphole series. For example, in the related Pd^{II} complex **8a** having P-CH_3 moieties, this angle reaches 86.7° (Figure 3). The consequence of this double-lock approach (C_3 chain and metal coordination) is a large red-shifted absorption of the $\mathrm{Pd^{II}}$ complex compared to that of all other biphosphole derivatives ($\lambda_{\max} = 479$ nm). Indeed, biphosphole appears to be a unique building block for tuning the HOMO–LUMO gap of π systems because their torsion angle can be controlled through varying the nature of the substituents on P (bridging or non-bridging) and using different chelating modes (1κ*P*,2κ*P* donors or P,P-chelates) of this subunit. Moreover, these structural modifications result in orthogonal covalent and coordination tuning: with non-bridging substituents, the $\mathrm{Au^{I}}$ complexes have the lowest HOMO–LUMO gap and the $\mathrm{Pd^{II}}$ complexes have the highest ones, whereas with the covalent bridging substituent, the $\mathrm{Pd^{II}}$ complexes display much lower HOMO–LUMO gaps than the $\mathrm{Au^{I}}$ complexes.

It was of great importance to show that these novel π-conjugated systems based on biphosphole synthons exhibit the required properties (high solid-state quantum yield, thermal stability, and suitable reversible redox potential) required for the application as materials in optoelectronic devices. All the structural modifications (Scheme 1) also have an impact on the emission properties of the 2,2′-biphosphole derivatives, both in solution and in the solid state. For example, amongst the $\mathrm{Au^{I}}$ complexes, only compounds having a C_3 aliphatic bridge (**7b,c**) between the two phosphorus atoms are emissive, probably because of the rotational restriction between the ground and excited states. Derivative **5c** exhibits an emission maximum in solution centered at $\lambda_{\max} = 585$ nm ($\Phi = 2\,\%$ versus fluoresceine). The same emission wavelength was observed using this compound as an emitting material for OLEDs having a classical structure (see the Supporting Information). Interestingly, this wavelength is complementary to that of 4,4-bis[2,2′-di(4-trifluoromethylphenyl)ethenyl]-1,1′-biphenyl (DPVBi), a communally used blue-emitting matrix. Therefore, biphosphole **5c** was used as a dopant of this blue matrix for the development of WOLEDs. Multilayered OLEDs were fabricated by co-evaporation of DPVBi and **5c** (2.2% doping rate; WOLED structure in Figure S3 in the Supporting Information). The device exhibits satisfying performances (external quantum yield: 0.5%; brigthness: 189 $\mathrm{cd\,m^{-2}}$ at 20 $\mathrm{mA\,cm^{-2}}$). The most important data is that the CIE (CIE = Commission International d′Eclairage) coordinates (0.34, 0.34) are almost similar to those of the perfect white emission (0.33, 0.33) because of a well-balanced dual emission from the DPVBI matrix and **5c**. This is the first time that a perfect white emission has been obtained with a phosphole-based dopant.[10]

In conclusion, exploiting the specific properties of biphospholes allows control of the torsion angles within π-conjugated systems. The fact that this novel series of P-based units within π-conjugated systems can be employed as materials in optoelectronics opens interesting perspectives towards the development of novel materials in plastic electronics.

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[1] a) (Eds.: K. Müllen, U. Scherf), *Organic Light Emitting Devices: Synthesis Properties and Applications*, Wiley-VCH, Weinheim, **2006**; b) Y.-J. Cheng, S.-H. Yang, C.-S. Hsu, *Chem. Rev.* **2009**, *109*, 5868–5923; c) T. J. Marks, *MRS Bull.* **2010**, *35*, 1018–1027; d) M. C. Gather, A. Köhnen, K. Meerholz, *Adv. Mater.* **2011**, *23*, 233–248; e) H. Usta, A. Facchetti, T. J. Marks, *Acc. Chem. Res.* **2011**, *44*, 501–510.

[2] a) J. Roncali, *Chem. Rev.* **1997**, *97*, 173–205; b) J. Roncali, *Macromol. Rapid Commun.* **2007**, *28*, 1761–1775.

[3] Intermolecular interactions in materials also impact the E_g. See: a) T. Yamamoto, H. Fukumoto, T. Koizumi, *J. Inorg. Organomet. Polym.* **2009**, *19*, 3–11; b) A. C. Grimsdale, K. L. Chan, R. E. Martin, P. G. Jokisz, A. B. Holmes, *Chem. Rev.* **2009**, *109*, 897–1091; c) A. Iida, S. Yamaguchi, *J. Am. Chem. Soc.* **2011**, *133*, 6952–6955; d) C. Xu, A. Wakamiya, S. Yamaguchi, *J. Am. Chem. Soc.* **2005**, *127*, 1638–1639; e) T. Baumgartner, *Chem. Eur. J.* **2007**, *13*, 7487; f) Y. Matano, T. Miyajima, T. Fukushima, H. Kaji, Y. Kimura, H. Imahori, *Chem. Eur. J.* **2008**, *14*, 8102.

[4] a) *Phosphorus-Carbon Heterocyclic Chemistry: The rise of a new domain* (Ed.: F. Mathey), Pergamon, Oxford, UK, **2001**; b) M. Hissler, P. Dyer, R. Réau, *Coord. Chem. Rev.* **2003**, *244*, 1–44; c) R. Réau, T. Baumgartner, *Chem. Rev.* **2006**, *106*, 4681–4727.

[5] a) M. O. Bevierre, F. Mercier, L. Ricard, F. Mathey, *Angew. Chem.* **1990**, *102*, 672–675; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 655–657; b) F. Laporte, F. Mercier, L. Ricard, F. Mathey, *J. Am. Chem. Soc.* **1994**, *116*, 3306–3311; c) M.-O. Bevierre, F. Mercier, F. Mathey, *New J. Chem.* **1991**, *15*, 545–550.

[6] a) M. Gouygou, O. Tissot, J.-C. Daran, G. G. A. Balavoine, *Organometallics* **1997**, *16*, 1008–1015; b) E. Robé, C. Ortega, M. Mikina, M. Mikolajczyk, J.-C. Daran, M. Gouygou, *Organometallics* **2005**, *24*, 5549–5559.

[7] a) P. Pyykkö, *Angew. Chem.* **2004**, *116*, 4512–4557; *Angew. Chem. Int. Ed.* **2004**, *43*, 4412–4456; b) P. Pyykkö, *Chem. Rev.* **1997**, *97*, 597–636; c) C. P. McArdle, S. Van, M. C. Jenning, R. Puddephatt, *J. Am. Chem. Soc.* **2002**, *124*, 3959–3965; d) S. Y. Yu, Z. X. Zhang, E. C. C. Cheng, Y. Z. Li, V. W. W. Yam, *J. Am. Chem. Soc.* **2005**, *127*, 17994–17995.

[8] a) O. Fadhel, Z. Benkö, M. Gras, V. Deborde, D. Joly, C. Lescop, L. Nyulászi, M. Hissler, R. Réau, *Chem. Eur. J.* **2010**, *16*, 11340; b) O. Fadhel, D. Szieberth, V. Deborde, C. Lescop, L. Nyulaszi, M. Hissler, R. Réau, *Chem. Eur. J.* **2009**, *15*, 4914–4924; c) C. Hay, M. Hissler, C. Fischmeister, J. Rault-Berthelot, L. Toupet, L. Nyulászi, R. Réau, *Chem. Eur. J.* **2001**, *19*, 4222.

[9] Note: Beside the torsion angles, the P-chemical modification can have an electronic impact on the HOMO–LUMO gap.

[10] a) B. W. D'Andrade, S. R. Forrest, *Adv. Mater.* **2004**, *16*, 1585; b) K. T. Kamtekar, A. P. Monkman, M. R. Bryce, *Adv. Mater.* **2010**, *22*, 572; c) B. W. D'Andrade, *Nat. Photonics* **2007**, *1*, 33.

[11] CCDC 835668 (**4b**), CCDC 835672 (**6b**), CCDC 835674 (**7b**), CCDC 835675 (**8a**), and CCDC 835676 (**9b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif