DOI: 10.1002/anie.201109205

Phosphole-Lipids

Bio-Inspired Phosphole-Lipids: From Highly Fluorescent Organogels to Mechanically Responsive FRET**

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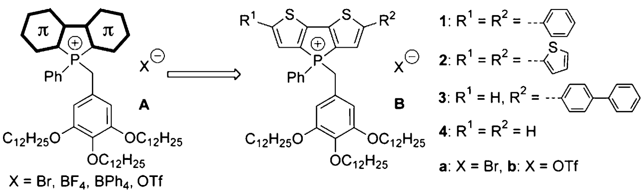
Heteroatom doping, that is the incorporation of B, Si, P, and S atoms, has been found to offer intriguing opportunities for the design of π-conjugated systems, and has thus attracted significant attention in the area of organic/bioelectronics.[1] Particularly phosphorus-doped materials have been identified as promising candidates for the development of advanced functional π-conjugated systems. Switchable and versatile phosphorus chemistry offers an effective channel for fine-tuning π-conjugated systems in terms of their photophysical properties (HOMO–LUMO gap, fluorescence quantum yield, charge transfer), redox properties, and electron affinity.[2]

In the same vein, well-organized micro-/nanostructures have been recognized as highly desirable for efficient energy, ion, and charge transport in organic electronics.[3] Among the intermolecular interactions that are commonly utilized to access such ordered systems (π–π interactions, H-bonding, and/or van der Waals forces), ionic interactions are a powerful force for long-range, high-order, and large-area self-assembly.[3] However, examples for the self-assembly of P-based conjugated systems to build these highly ordered systems are extremely sparse in the literature.[4]

We have recently reported novel stimuli-responsive phosphole-lipids (Scheme 1 A) that exhibit liquid-crystalline behavior arising from the combination of the amphiphilic features of lipids and the electronic features of conjugated phospholes.[4a] Herein, we now report on novel, highly fluorescent amphiphilic organogels prepared by further molecular engineering of the phosphole-lipid system. Since the unique structural features of the phosphole materials are distinctly different from those of classic conjugated organogels with planar structures,[5,6] we have focused on structure–property relationships with respect to both fundamental aspects and practical applications in this study. In particular, a unique mechanically responsive energy transfer was uncovered by our studies that highlights the light-harvesting capabilities of this bio-inspired self-assembled system.



Scheme 1. A) Previously reported ionic liquid-crystal systems. B) New ionic organogel materials.

The series of symmetrically and dissymmetrically π-extended phospholium salts for this study (**B**) was synthesized by procedures similar to those reported previously (Scheme 1; see the Supporting Information for details). The identity of all new compounds was confirmed by ^1H, ^{13}C, and ^{31}P NMR spectroscopy, high-resolution mass spectrometry, and elemental analysis. The different conjugated phospholium backbones and counteranions ($Br^-$and OTf^-) were chosen to reveal potential structural effects on the self-assembly and photophysical properties of the systems.

The photophysical properties of the new phospholium salts are summarized in Table 1. Compounds **1**–**3** with an extended backbone show very strong fluorescence in $CHCl_3$ arising from intramolecular charge transfer (ICT) from the terminal aryl groups to the phospholium core.[4a] The ICT emission energy decreases with the increasing electron-donating ability of the aromatic substituents in the order: **4**(blue) > **3**(light green) > **1**(green) > **2**(orange). Multiexponential decay profiles and broadened emission spectra at lower concentration (10^{-5} M) furthermore support the structural flexibility of the systems, which was expected in analogy to the properties of the known phosphole-lipids **A** (see the Supporting Information).[4a]

In stark contrast to the liquid-crystal features of the previously reported non-extended phospholium salts **4a**,**b**,[4a]

Table 1: Photophysical properties of **1a**,**b**, **2a**,**b**, and **3a**.

	Solution[a]		Gel[d]	Solid[e]
	λ_{abs} (ε)[b] [nm]	λ_{em} (φ[c]) [nm]	λ_{em}(φ[c]) [nm]	λ_{em}(φ[c]) [nm]
1a	438 (18050)	535 (77%)	548 (81%)	533 (30%)
1b	438 (10420)	535 (70%)	541 (70%)	534 (60%)
2a	463 (46880)	577 (79%)	–	579 (14%)
2b	464 (30310)	577 (53%)	578 (60%)	567 (20%)
3a	417 (28 920)	519 (57%)	–	535 (40%)

[a] Measured in $CHCl_3$ (10^{-5} M). [b] ε ($M^{-1}cm^{-1}$): molar absorption coefficient. [c] Fluorescence quantum yield determined by a calibrated integrating sphere system. [d] 5.0×10^{-3} M in hexane at room temperature. [e] Drop-cast film.

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[**] Financial support by NSERC of Canada and the Canada Foundation for Innovation (CFI) is gratefully acknowledged. We also thank Alberta Ingenuity, now part of Alberta Innovates-Technology Futures, as well as Talisman Energy for a graduate scholarship (Y.R.). We are grateful to Prof. Dr. T. Sutherland, Prof. Dr. C. Berlinguette, Prof. Dr. B. Heyne, and Dr. Q. L. Ma for their help with using instruments. FRET = fluorescence resonance energy transfer.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201109205.

1a,**b** and **2b** with two extended aromatic groups form highly fluorescent gels in hydrocarbon solvents (cyclohexane, hexane, and heptane; Figure 1). Remarkably, **1b** can form transparent gels in heptane even at a low critical gel concentration (CGC) of 2.5 mM (**1a**: 5.0 mM in hexane, **1b**: 4.3 mM in hexane, **2b**: 4.6 mM in hexane; see the Supporting Information), which is comparable to that of classic π-conjugated organogels with highly planar backbones, such as oligo-*p*-phenylene vinylenes.[5,6] The gelation temperature (T_{gel}) of compounds **1a**,**b** and **2b** in hexane (5.0 mM) is 40 °C, 43 °C, and 41 °C, respectively, and was determined by the "inverse-flow" method. As for the compounds with a truncated conjugated core, only **4b** forms a partial gel in heptane at room temperature. In addition, the dissymmetric biphenyl-substituted phosphole-lipid **3a** did not display any gel formation in either hydrocarbon solvent; compound **2a** with a bromide counterion is only partially soluble in these solvents. The observations suggest that only phosphole-lipids having molecular structures with the "correct" arrangement of peripheral aromatic substituents and counterions self-assemble during the gelation process. In addition, sonication was found to enhance the gelation of the collapsed gels of **1a**,**b** and **2b**. The presence of one-dimensional (1D) microfibers and bundled fiber structures for the organogels of **1a**, **1b**, and **2b** in hydrocarbon solvents (cyclohexane, hexane, and heptane) was unequivocally confirmed by confocal fluorescence microscopy (see Figure 1 d,e and the Supporting Information). Interestingly, the organogels of **1a**,**b** and **2b** also tend to form large aggregates on mica, as observed during the scanning electron microscopy (SEM) experiments (see Figure 2 and the Supporting Information).

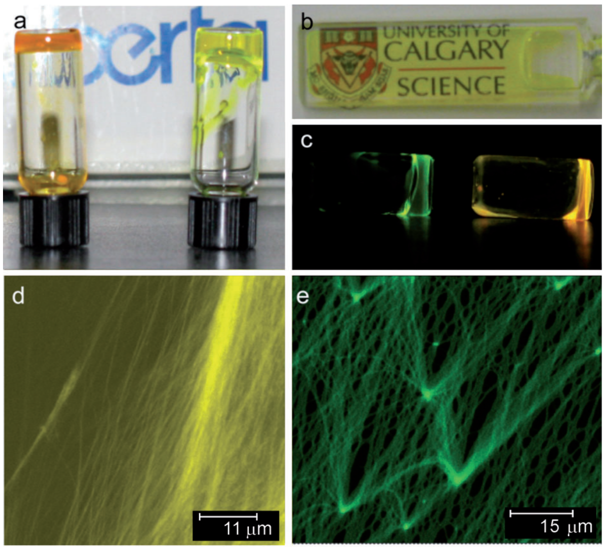

Figure 1. a) Organogels of **2b** (left) and **1b** (right). b) Transparent gel of **1b**. c) Fluorescence images of organogels of **1b** (left) and **2b** (right). d, e) Confocal fluorescence microscopy of the gels of **2b** and **1a** (5.0×10^{-3} M in hexane at room temperature).

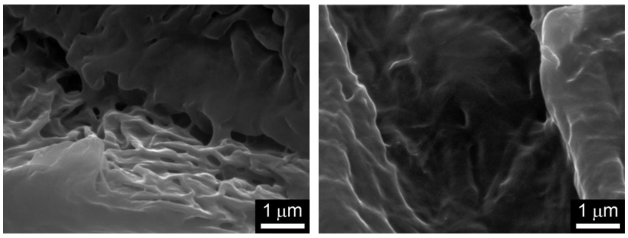

Figure 2. Scanning electron micrographs (SEM): a) dried gel of **1a** from hexane; b) dried gel of **2b** from hexane.

The heteroatom-specific bulky phospholium center endows the organogels with very high fluorescence quantum yields (**1a**: $\varphi = 81\,\%$, **1b**: $\varphi = 70\,\%$, and **2**: $\varphi = 60\,\%$). Generally, the emission of the organogels (5.0×10^{-3} M in hexane) is significantly narrowed and red-shifted compared to the emission of the corresponding diluted solutions (ca. 10^{-5} M in hexane, Figure 3) and the solid state (Table 1). Moreover, we found that **1a**,**b**, **2b**, and **3a** also exhibit significantly red-shifted emission spectra (**1a**: $\Delta\lambda = 12$ nm, **1b**: $\Delta\lambda = 7$ nm, **2b**: $\Delta\lambda = 15$ nm **3a**: $\Delta\lambda = 16$ nm) when the concentration is increased from 10^{-6} M to 10^{-3} M in hexane (see inset in Figure 3 and the Supporting Information). By contrast, variable-temperature optical spectroscopy of **1a**,**b** and **2b** (5.0 mM in hexane, see the Supporting Information) revealed no significantly red-shifted and broadened emission upon moving from the liquid (60 °C) to the gel phase (30 °C). This feature is distinctly different from the organogels with planar conjugated backbone (such as oligo-*p*-phenylenevinylenes and acenes) that commonly exhibit an enhanced red-shifted aggregate- and a weakened monomer-absorption band.[5,6] These observations indicate that no strong π–π interactions occur in the gel phase of the novel phosphole-lipids. Therefore, the emission differences of these compounds in the gel state and in solution are very likely due to conformation changes that predominantly affect the excited state of the molecules, either through intramolecular charge transfer or σ*–π* hyperconjugation.[7] The fact that the solid-state emission of **1a**,**b** and **2b** is blue-shifted relative to the gel-state emission also suggests the existence of different molecular conformations in the solid state (Table 1). Dynamic

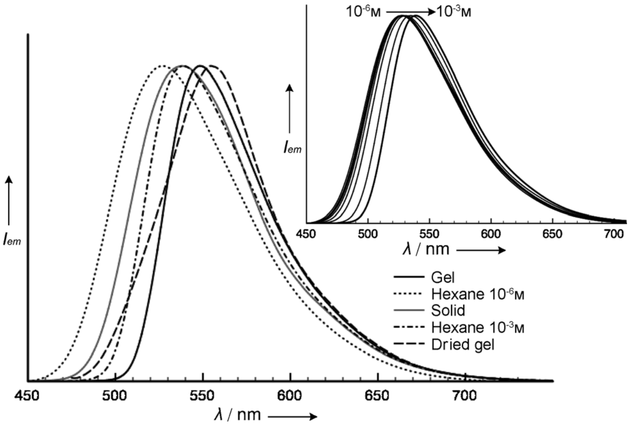

Figure 3. Emission spectra of **1a** under different conditions. Inset: Concentration-dependent absorption spectra of **1a** (1.2×10^{-3} to 1.2×10^{-6} M in hexane).

fluorescence experiments further indicate that the different emission properties of the systems under different conditions (solution, solid state, gel) indeed result from different excited states (see the Supporting Information).

Powder X-ray diffraction experiments (PXRD, see the Supporting Information) were carried out with the dried gels and revealed one strong peak in the low-angle region (**1a**: $d = 28.3$ Å, **1b**: $d = 25.6$ Å, and **2b**: $d = 25.9$ Å). However, the relatively weak and broad peaks of the dried gels cannot be used to make unambiguous assignments. The emission spectra of the dried gels of **1a**,**b** and **2b** are also different from those of the corresponding hexane gels (see Figure 3 and the Supporting Information). Therefore, the X-ray diffraction patterns could not be utilized to study the molecular organization of the gels. Based on the current studies, however, instead of π–π interactions, ionic interactions are believed to be the major driving force for the formation of the highly fluorescent organogels, which is supported by the variable-concentration NMR studies.[8a] A plausible molecular organization for the organogels is proposed in Figure 4. In hydrocarbon solvents, the solvophobic effect allows the phosphole-lipids to form inverse rodlike structures in which the ionic conjugated heads aggregate through ionic interactions inside the fibers and the hydrophobic tails point out into the solvent (Figure 4, top view); this is complementary to the aggregation of amphiphilic molecules in aqueous solution.[9] Besides, the intermolecular interactions of the two peripheral aromatic (phenyl or thienyl) groups of the dithieno core could further stabilize these 1D fiberlike structures (Figure 4, side view).[8b]

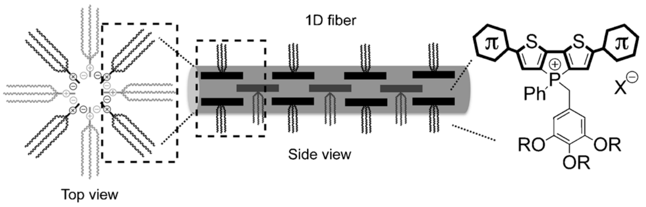

Figure 4. Plausible molecular organization of the 1D fibers of **1a**,**b** and **2b**.

In order to investigate the light-harvesting capabilities of the new systems, the potential energy transfer between phosphole-lipids **1a**,**b** as the donors and Rhodamine B as an acceptor was studied in $CHCl_3$ (see the Supporting Information). Both **1a** and **1b** show fluorescence resonance energy transfer (FRET) with moderate efficiencies of 43 % and 46 %, respectively, at a donor/Rhodamine B ratio of 1:1 in $CHCl_3$. Because of the low solubility of Rhodamine B in the hydrocarbon solvents used for this study, the energy-transfer process was studied in the solid state instead of the gel state. Figure 5 shows that the donor emission of **1a** is partially quenched when the drop-cast film was doped with 25 % mol of Rhodamine B. Interestingly, upon mechanical grinding of the film, the donor emission of **1a** was further quenched significantly. Concurrently, the emission decay of donor **1a** in the mechanically ground film was shortened, indicating the presence of a nonradiative energy-transfer process (Figure 5, inset). Subsequent thermal annealing (5 min at 90 °C) resulted in the recovery of the original emission spectrum. A film containing **1b** and Rhodamine (3:1) also exhibits similar mechanically responsive energy-transfer features indicating that the process is independent of the counteranion (see the Supporting Information).

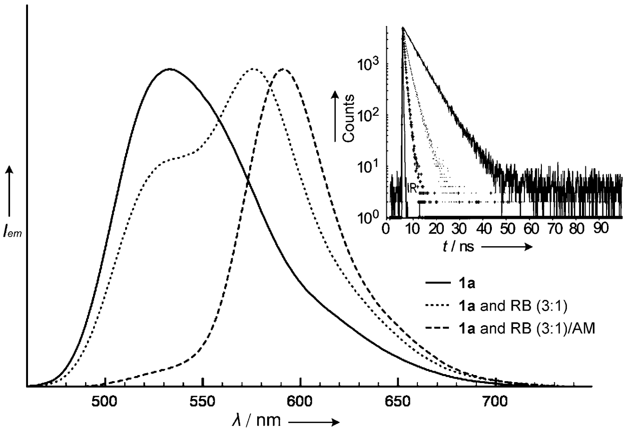

Figure 5. The solid-state emission spectra of **1a** in the absence (solid line) and presence of Rhodamine B (3:1) (dotted line) before mechanical grinding (BM) and after mechanical grinding (AM) (3:1) (dashed line). Inset: Corresponding emission decay (excitation at 466 nm and monitoring at 533 nm) in the solid state. Solid line: **1a**, dotted line: **1a** and Rhodamine B (3:1) BM, crosses: **1a** and Rhodamine B (3:1) AM, IR: instrument response decay.

Encouraged by this mechanically responsive FRET, we envisioned that the mechanically responsive emission of the phosphole-lipid system could be further amplified through the energy transfer from the donor to a similar acceptor species. We thus chose **4b** as the donor (blue emission) and **2b** as the acceptor (orange emission) in order to amplify the stimulus-responsive signal. The efficient spectral overlap between the emission of **4b** and the absorption of **2b** promised for efficient FRET in the solid state. The drop-cast film containing **4b** and **2b** (100:1) exhibited a typical blue emission of **4b** ($\lambda = 460$ nm) with a broader red-shifted tail (Figure 6). However, upon mechanical grinding, the fluorescence of the doped film shifted to orange. Figure 5a shows that the donor emission of the ground film is considerably quenched; the emission of the acceptor **2b** ($\lambda = 567$ nm) is the main component after grinding. Importantly, the blue emission can be fully recovered by thermal annealing of the ground film (5 min at 90 °C), and this process can remarkably be repeated several times.

It is well known that FRET can occur over distances of up to 100 Å between donor and acceptor.[10] But more importantly, the FRET efficiency is highly dependent on the donor–acceptor distance, which makes such intermolecular process very useful for the sensing of external stimuli, particularly in the application toward mechanical responses.[11] Based on our studies, this mechanically responsive FRET is believed to be mainly due to changes in the distance between the donor and the acceptor. In the drop-cast film, the electrostatic repulsion prevents strong intermolecular interactions between the bulky phospholium donor (**4b**) and the acceptor (**2b**) species,

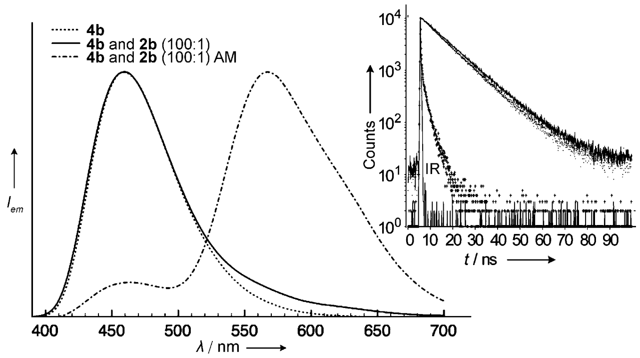

Figure 6. Emission of the doped film containing **4b** and **2b** (100:1) before mechanical grinding (BM) and after mechanical grinding (AM). Insert: Corresponding emission decay (excitation at 374 nm and monitoring at 460 nm) in the solid state. Solid line: **4b**, dotted line: **4b** and **2b** (100:1) BM, crosses: **4b** and **2b** (100:1) AM, IR: instrument response decay.

leading to less efficient energy transfer. Therefore, the blue emission of the donor (**4b**) is mainly observed. Upon mechanical force, changes in the intramolecular conformation and phase separation likely decrease the intermolecular distance between donor and acceptor, which in turn enhances the efficiency of the energy-transfer process. The PXRD pattern also suggests a disturbed lamellar organization of the donor upon mechanical grinding of the doped film (**4b/2b** 100:1; see the Supporting Information). Moreover, it has been demonstrated before that efficient exciton migration could be preserved in organogels, nanoparticles, and even in amorphous solids.[5,6,12] It is therefore inherently plausible that both efficient exciton migration (donor–donor) and the enhanced energy transfer (donor–acceptor) work together to enhance the orange emission of the acceptor upon mechanical grinding as a result of created trap sites. The changes in the dipole orientation of the donor and acceptor that could also affect the energy-transfer rate could not be fully ruled out at this stage.[8] Because of the flexible structural features of the phosphole-lipids, thermal annealing can provide sufficient energy for conformational changes that increase the spatial vicinity of donor and acceptor, which consequently prevent efficient energy transfer to occur.

In conclusion, highly fluorescent ionic organogels were obtained through the combination of the electronic nature of extended π-conjugated phospholes and the amphiphilic nature of lipids. The systematic studies revealed that the ionic interactions are the main driving force for the gelation process. Both the conjugated backbones and counterions have a considerable effect on the self-assembly of the systems. In the energy-transfer studies, efficient FRET could be observed between the phospholium system and Rhodamine B in both solution and the solid state. As a new mechanochromic concept for the amplification of the emission signal in this phosphole-lipid system, a significant emission shift (blue to orange) can be observed for the donor–acceptor system (100:1) which has a FRET that is responsive to external stimuli (mechanical grinding and thermal annealing).

Received: December 29, 2011

Keywords: energy transfer · fluorescence · mechanochromism · organogels · phosphorus heterocycles

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