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Zinc(II)-operated intramolecular charge transfer fluorescence emission in pyrene-2,2′-bipyridine conjugated molecular rods

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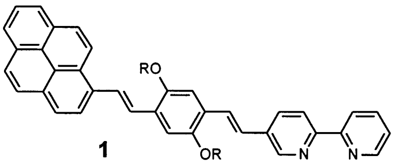
Abstract—The design and synthesis of two conjugated pyrene-2,2′-bipyridine linear rods is described. Zn(II) ion complexation allows the formation of a highly polar emissive excited state through efficient photoinduced intramolecular charge transfer.

The design of molecular systems capable of performing the transduction of recognition events into fluorescence signal represents a fascinating challenge for the development of chemosensors and photonic devices.[1–4] Recently, two-component molecules displaying ionic-input-operated fluorescent ON/OFF switching were demonstrated to work as molecular scale logic gates.[4] The salient functional feature pertaining to these systems is the triggering of intramolecular photoinduced electron transfer (PET) upon protonation or metal ion binding at the nitrogen sites of the ligand subunit,[4,5] the resulting fluorescence quenching effect providing the optical output in response to the chemical input. Inherently, the efficient charge separation process occurring in these systems should provide a further readable output in the form of an electrical signal. Therefore the combination of fluorescent switching and photoconductivity generation, both processes being simultaneously driven by a chemical event, could be envisaged at the single molecule level. To this end, the design of wire molecular switches in which the fluorophore and receptor sites are rigidly connected by a conjugated bridge could represent a promising approach toward molecular systems with well-defined shape and length, exhibiting high electronic communication and geometrically controlled intramolecular charge transport properties. Rigid-rod conjugated molecules have attracted considerable interest as photoactive components on which to base the construction of functional supramolecular nanostructures.[6]

Herein, we present the design and the synthesis of two highly fluorescent conjugated pyrene-2,2′-bipyridine (bpy) derivatives, **1** and **2**, and their preliminary fluorescence properties. Analogous systems with outstanding excited state properties have been published in the literature.[7] The introduction of a vinylene- or ethynylene-phenylene group as a spacer unit between the bpy and pyrene moieties was anticipated to provide for high fluorescence efficiency, as compared to alkyl-substituted pyrene derivatives.[5,8–10] Indeed we observed previously that direct linking of the pyrene chromophore to the bpy coordinating unit could lead to highly fluorescent systems,[9] due to the effective stabilization of the long-axis polarized $^{1}\mathrm{L}_{a}$ transition of pyrene. The 2,5-disubstituted-1,4-phenylene unit as a central aromatic bridge can be substituted with a variety of pendant functional groups in order to further endow these systems with improved solubility[11] or directed self-assembling properties.[12]



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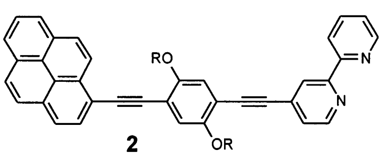

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Keywords: fluorescence; polycyclic aromatic compounds; complexation; electron transfer; molecular devices.

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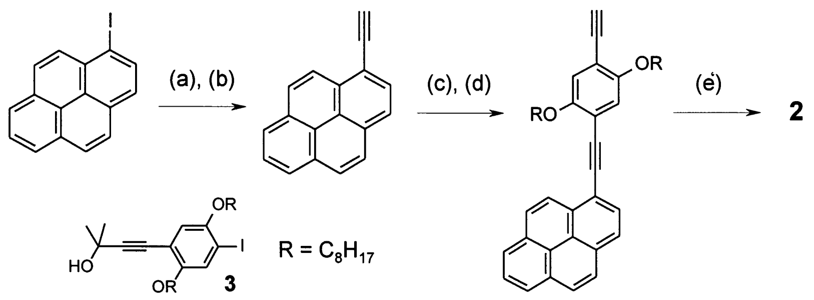

Scheme 1. (a) HC≡C(CH$_3$)$_2$OH (1.2 equiv.), Et$_2$NH, [Pd^{II}(PPh$_3$)$_2$Cl$_2$] (2.5 mol%), CuI (1.5 mol%), 50°C, 20 h, 70%; (b) NaOH (excess), toluene, reflux, 2 h, 90%; (c) **3** (0.7 equiv.), Et$_2$NH, [Pd^{II}(PPh$_3$)$_2$Cl$_2$] (11 mol%), CuI (11 mol%), 50°C, 18 h, 90%; (d) NaOH (excess), toluene, reflux, 2 h, 80%; (e) 4-bromo-2,2′-bipyridine (1.1 equiv.), Et$_2$NH, [Pd^{II}(PPh$_3$)$_2$Cl$_2$] (7 mol%), CuI (15 mol%), 30°C, 20 h, 22%.

Table 1. Selected photophysical data for compounds **1** and **2** and their Zn(II) complexes

	Toluene			THF			Acetonitrile		
	λ_{max}[a] (nm)	ϕ_{fluo}	λ_{max}[b] (nm)	λ_{max}[a] (nm)	ϕ_{fluo}	λ_{max}[b] (nm)	λ_{max}[a] (nm)	ϕ_{fluo}	λ_{max}[b] (nm)
1	431	0.81	493	430	0.82	493	430	0.72	493
2	411	0.52	442	411	0.68	442	414	0.72	442
1-Zn^{2+}	455	0.64	563[c]	455	0.28	614	455	–[e]	–[e]
2-Zn^{2+}	420	0.51	487[d]	420	0.40	578	420	–[e]	–[e]

[a] Absorption maxima.

[b] Fluorescence emission maxima.

[c] 637 nm in dichloroethane, 642 nm in butyronitrile.

[d] 595 nm in dichloroethane.

[e] Quenched emission.

The synthesis of compound **1** was performed according to a one-pot procedure[13] involving two Wittig reactions between the disphosphonium salt derivative of 1,4-bis-(bromomethyl)-2,5-bis(octyloxy)benzene[14] and pyrenecarboxaldehyde and 2,2′-bipyridine-5-carbaldehyde.[15] The synthesis of **2** involved a sequence of Pd-mediated cross-coupling reactions of ethynyl derivatives with the corresponding haloarenes, as outlined in Scheme 1.[9a,16]

Both compounds exhibit broad, red-shifted UV–vis absorption and fluorescence emission spectra (Table 1) relative to those of pyrene-bpy derivatives in which the tether between the two terminal subunits is a single C–C bond,[9] which is consistent with an extended conjugation in the ground and excited state. They also exhibit high fluorescence quantum yields in agreement with a singlet emitting state possessing a predominant ^1L_a character (Table 1). Addition of ZnCl$_2$ or Zn(BF$_4$)$_2$ to solutions of **1** and **2** induced a red shift of the lowest energy transition band in the UV–vis spectrum (+25 nm for **1**), the value of the bathochromic shift being independent of the solvent nature. The modification of the absorption spectrum upon gradual addition of Zn(BF$_4$)$_2$ was used to monitor the metal complexation equilibrium, which indicated the formation of a 1:1 complex with a stability constant l g K of 5.5±0.2 for both ligands in THF as solvent.[17] A dramatic modulation of the fluorescence emission characteristics was observed upon addition of Zn^{2+} ions into solutions of the ligands (Table 1, Fig. 1). In THF, a considerable bathochromic shift of the fluorescence maximum of about 120 and 140 nm was observed for compounds **1** and **2**, respectively, along with a relatively small drop in fluorescence quantum yield. In the polar solvent acetonitrile, addition of zinc(II) resulted in the quasi total quenching of fluorescence emission. In all the solvents investigated, the absorption and emission features of the free ligands were totally restored upon addition of 2,2′-bipyridine as competing ligand, indicating that the Zn(II)-induced spectral changes are fully reversible. Fluorescence spec-

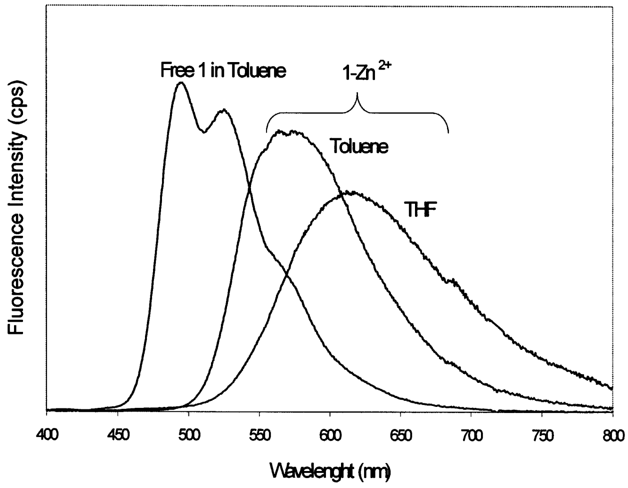

Figure 1. Corrected fluorescence emission spectra of the free ligand **1** in toluene, and of its Zn(II) complex in toluene and THF (ligand concentration: <10^{-6} M, metal concentration: 10^{-4} M, excitation 400 nm).

troscopy of the $ZnCl_2$ complexes of **1** and **2** was investigated in solvents of different polarity in order to confirm the occurrence of electron transfer as quenching mechanism. As illustrated in Fig. 1 for compound **1**, the emission maximum was observed to shift dramatically to the red when the polarity was increased (Table 1). This solvatochromic effect is typical of donor/acceptor molecules displaying a highly polar excited state due to the occurrence of photoinduced intramolecular charge transfer (ICT).[18] Upon zinc complexation, the terminal bpy ligand in compounds **1** and **2** becomes a strong electron withdrawing group, which promotes ICT state formation. From the dependence of the emission maximum on the solvent polarity factor, a line was obtained for the zinc complexes of **1** and **2** using the Lippert–Mataga equation,[18] allowing us to obtain a value for the dipole moment of the excited state of the zinc complexes greater than 25 D. This behaviour is consistent with that reported for a family of Zn(II) complexes of bipyridine derivatives substituted with a strong donor group which show large dipolar nonlinearities.[19] Furthermore, when $Zn(BF_4)_2$ was used instead of $ZnCl_2$, the fluorescence maximum in the spectrum of **1** shifted from 614 to 642 nm in THF, consistent with the higher Lewis acidity of the zinc ion bearing the tetrafluoroborate counteranions. This feature provides a further method to control the fluorescence emission properties of these systems. Compounds **1** and **2** are rigid rod shaped complexing molecules which are shown not only to function as fluorescent switches but also to operate directional photoinduced charge separation upon Zn^{2+} ion binding. They represent promising photoactive π-systems for the development of photonic and electronic devices. We are currently investigating the photophysical properties of these systems using time-resolved ultrafast spectroscopy.

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13. Actually, this procedure led to the obtention of compound **1** in a mixture of the bis-pyrenyl and bis-bipyridyl symmetrical derivatives. All three compounds could be easily separated using column chromatography. Compound **1** was obtained in a pure all-*trans* form (20% isolated yield), as confirmed by ^1H NMR spectroscopy and X-ray structural analysis. **1**: ^1H NMR ($CDCl_3$, 400 MHz) δ 0.93 (m, 6H), 1.37 (m, 16H), 1.6 (m, 4H), 1.9 (m, 4H), 4.1 (m, 4H), 7.21 (s, 1H), 7.31 (s, 1H), 7.33 (m, 1H), 7.66, 7.22 (dd, $J_{AB}=16$ Hz, 2H), 7.84 (t, 1H), 8.10 (m, 8H), 8.30, 7.68 (dd, $J_{AB}=16.0$ Hz, 2H), 8.35 (d, 1H), 8.44 (d, 2H), 8.53 (d, 1H), 8.70 (d, 1H), 8.82 (d, 1H). MS (IE) *m/z* 740 [M^+]. Anal. calcd for $C_{52}H_{56}N_2O_2$: C, 84.28; H, 7.62; N, 3.78. Found: C, 83.88; H, 7.23; N, 3.93.
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16. **2**: ^1H NMR ($CDCl_3$, 200 MHz) δ 0.82 (m, 6H), 0.92 (m, 24H), 4.14 (q, 4H), 7.12 (s, 1H), 7.20 (s, 1H), 7.43 (m, 2H), 7.83 (t, 1H), 8.12 (m, 8H), 8.48 (m, 1H), 8.60 (m, 1H), 8.69 (m, 2H), 8.85 (d, 1H); MS (FAB^+) *m/z* 737.5 [$M+H^+$]. Anal. calcd for $C_{52}H_{52}N_2O_2$: C, 84.75; H, 7.11; N, 3.80. Found: C, 84.12; H, 7.07; N, 3.89.
17. Time-resolved laser spectroscopy measurements (temporal resolution 50 ps) allowed us to obtain monoexponential fluorescence decays for **1** and **2** in the presence of an excess of either $ZnCl_2$ or $ZnBF_4$, which confirmed the occurrence of a single 1:1 species in THF solution. In more polar coordinating solvents, such as methanol or acetonitrile, multiexponential decays were obtained when the emission was monitored at the red shifted low emitting band of the complex. In this case, electrospray mass spectrometry pointed to the formation of the 1:1 complex as the major component, along with small amounts of bis-ligand Zn(II) complex species.
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