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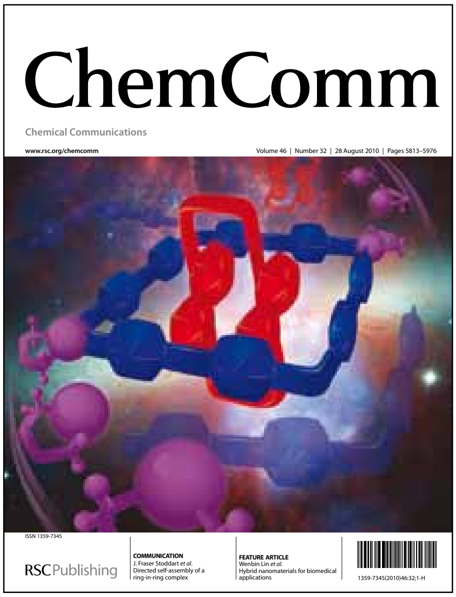

ChemComm
Chemical Communications
www.rsc.org/chemcomm Volume 46 | Number 32 | 28 August 2010 | Pages 5813–5976
ISSN 1359-7345
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Reversible luminescence switching between single and dual emission of a bipyridinium-type organic crystals

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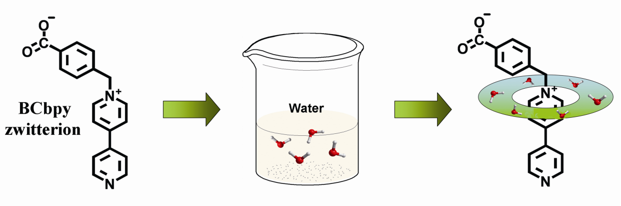
Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

An excitation-wavelength-dependent luminescence behavior of a bipyridinium derivative, together with its luminescence switching between single- and dual-emissions upon reversible solid state structural transformation has been represented.

The preparation of multifunctional luminescent materials by assembly of organic compounds in ordered molecular arrangements is a subtle but hot topic in organic solid-state chemistry.[1] One of the most important issues in this area is how to efficiently control solid-state luminescence behaviors and achieve reversible luminescence switching for both fundamental research and practical applications.[2] A promising approach is to alter molecular conformation and packing mode through external stimuli, such as temperature, mechanical pressure and vapor etc.[3] However, examples with efficient and reliable switching of solid-state luminescence are limited due to the difficulty in solid-state structural conversion.[3,4] Especially, due to the restriction of molecular species and crystal engineering, most early established models only focused on on/off or color switching based on single-color emission,[3-5] the precise control of single- and multi-fluorescence switching of the same molecule in different homogeneous aggregation states has not been established despite their great advantages in white light emission materials and biological sensing applications.[6-7]

To achieve multiple photoluminescence, a major challenge exists in how to judiciously design the molecular system bearing different emitting states. Different from a few metal coordination compounds (eg. Ru(II) or Ir(III) polypyridine-based complexes), which can possess two simultaneously emissive excited states associated with the MLCT transition,[8] stable multiple excited states (except for exciplex or excimer states) commonly means a combination of multicomponent emitters in a matrix for most organic materials, which obviously increase the chance of the energy loss by non-radiative pathways via intra- or intermolecular connection in solid states or concentrated environments. For this reason, maintaining their emission efficiencies and achieving precise luminescent switching with definite structural variations are challenging. Although several single molecules with multiple fluorescence emission have been successfully explored in solutions or films,[9] precise crystallographic study on single-component multiple emissive materials, which may exclude the possibility of multi-emission origining from various molecular conformations,[10] was not performed.



***Scheme 1**.* Molecular structure of the BCbpy zwitterion and a schematic representation of the self-assembly method of **Form1**.

Recently, we have developed a new bipyridinium molecule with 2-carboxybiphenyl groups, and observed an interesting proton-triggered fluorescence switching behavior.[11] It appears that the incorporation of carboxyl groups into the disubstituted 4,4′-bipyridinium molecular system may greatly improve the luminescence properties of 4,4′-bipyridinium derivatives, giving rise to a long-wavelength emission in the visible range based on the intramolecular charge transfer (ICT) mechanism. Along this line, we extend our study to a mono-substituted bipyridinium zwitterion BCbpy (HBCbpyCl = 1-(4-carboxybenzyl)-4,4′-bipyridinium chloride, Scheme 1). Attractively, not only a dual fluorescence emission has been detected in aqueous solution and the crystalline state for this single zwitterionic molecule, but also a reversible luminescent switching between single and dual emissions by the variation

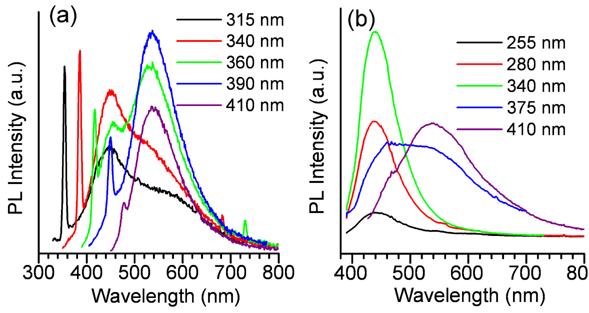


Fig. 1 Excitation-wavelength-dependent fluorescence emission spectra of BCbpy molecule in aqueous solution (a) and **Form 1** in the solid state (b). The sharp peaks in (a) are Raman lines.

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† Electronic Supplementary Information (ESI) available: Synthesis, characterization and other detailed experimental data. CCDC 822542-822543. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x

in molecular stacking mode has also been established.

The fluorescence emission spectra of the zwitterionic BCbpy in aqueous solution show an intense emission band at 450 nm with a small shoulder around 540 nm upon excitation at 315 or 340 nm. With increasing excitation wavelengths, the intensity of the short-wavelength emission gradually decreases, while the long-wavelength emission gains intensity and becomes dominant. When the excitation wavelength is further increased, the intensity of long-wavelength band also begins to decrease (Fig. 1a). To clarify whether this wavelength-dependent behavior is related to different conformers of the molecule as common discussion on organic small molecules,[10,12] crystal engineering approach is considered and column-like single crystals of BCbpy zwitterion (BCbpy·6H_2O, **Form1**) have been sucessfully grown from an aqueous solution. X-ray single crystal analysis reveals that there is only one BCbpy molecule in the asymmetric unit (Fig. 2a and Fig. S1 in ESI), suggesting that BCbpy owns homogeneous molecular conformation in **Form1**. Very interesting, the bulk crystals exhibit similar excitation-wavelength-dependent fluorescence behavior to that in aqueous solution, which can be clearly observed even by naked eye (Fig. 2e), blue and almost-white emissions can be observed under a UV lamp with the wavelength of 254 or 365 nm, respectively. This observation clearly excludes the possibility that the wavelength-dependent behavior of BCbpy molecule origins from the multiple molecular conformations, being distinct from the common red-edge effect of some organic molecules.[10]

The solid-state luminescence spectra provide definite support for this excitation-wavelength-dependent dual emission behavior of **Form1** (Fig. 1b). When excited at wavelengths below 340 nm, **Form1** exhibits an emission centered at 438 nm, which is about 12 nm blue shift with respect to the short-wavelength emission observed in aqueous solution. As the excitation wavelength increased further, the short-wavelength band shows a decrease in emission intensity, accompanied by the development of the long-wavelength emission band centered at 537 nm. The fluorescence excitation spectra monitored at 438 and 540 nm show structureless broad bands with the excitation maxima at 338 and 370 nm respectively (Fig. S2, †ESI), suggesting that there are two different emission transitions in the present luminescence system. The emission peak at 438 nm is similar to that observed for pure 4,4′-bipyridine (Fig. S3, †ESI), and thus is assigned to the intramolecular π···π* transition of the bipyridinium moiety. The emission band around 537 nm may correspond to the intramolecular charge transfer (ICT) emission as we previously reported for the disubstituted bipyridinium derivative,[10] which can be confirmed by solvent-dependent emission behavior. Upon decreasing solvent polarity from water to MeCN (Fig. S4, †ESI), this long-wavelength band becomes invisible, only a dominant emission band appears at 457 nm. Such a solvent-dependent emission behavior is typical for ICT fluorescence.[13] To achieve multi-color fluorescence emission in a single organic molecule, a typical strategy is to combine two different fluorophores through covalent bond linkage. However, successful examples are rare because energy transfer usually quenches one or more of the emission pathways.[9b,14] The present work suggests that the appropriate quaternary ammonium modification on nitrogen-containing organic single-color emitter may tune the electronic structure of molecular system, achieving the multi-color luminescence emission through introducing additional ICT emission.

One interesting structural feature of **Form1** is that there are strong hydrogen-bonding interactions between the lattice water molecules and BCbpy. The water molecules are linked together into an infinite 2D water layer composed of 14-membered water rings (Fig.2b). Adjacent water layers stack in -ABAB- mode along the *b*-axis and are linked by carboxylate oxygen atoms through the hydrogen bonding interactions into a 3D porous supramolecular framework. Each BCbpy molecule is situated in the center of the 14-memebred water ring, and offers pyridyl nitrogen and carboxylate oxygen atoms as proton acceptor to form hydrogen bonds with the molecules within adjacent water layers, resulting in that BCbpy itself is locked in the cages of the 3D framework (Fig. 2c-d). Such an interesting water molecule-surrounded polar environment around BCbpy molecule may provide some degree of support for the consistent observation on the luminescence behaviors in aqueous solution and in the solid state.

Remarkably, as the crystals are ground at room temperature, the blue-color emission excited at 254 nm gradually fades away.

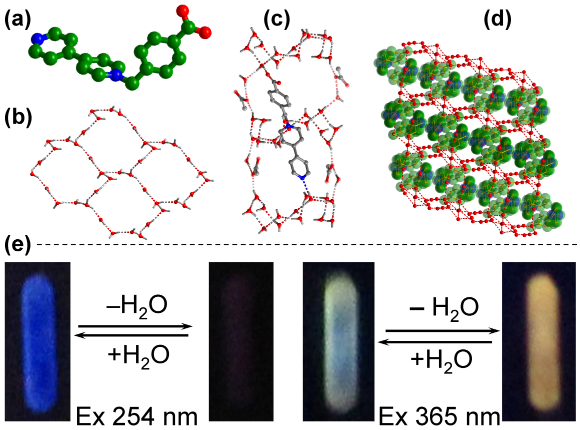

Fig. 2 (a) BCbpy in the structure unit of **Form1**. (b) 2D water layer composed of 14-membered water rings. (c) The BCbpy molecule in the hydrogen-bonded water cages. (d) 3D hydrogen-bonded porous water framework inside which the BCbpy molecules sit. (e) Fluorescence images of the original and dehydrated samples of **Form1** under a UV lamp with the wavelength of 254 or 365 nm. The blue emission is weaker as the excitation wavelength of 254 nm is not optimal.

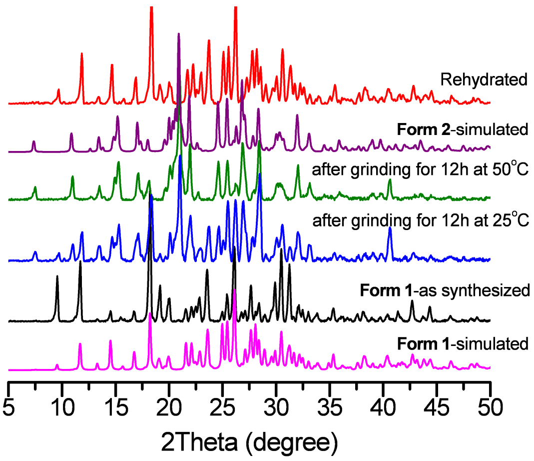

Fig. 3 XRPD patterns show the reversible transformation of **Form1** and **Form2** via dehydration-rehydration.

After additional grinding for 12 h at 50 °C, the blue emission finally disappears, and a new phase **Form2** only with single yellow-color emission can be obtained. Upon keeping **Form2** under moisture condition for 48 h, the sample is reverted to the initial phase with dual fluorescence emission. Elemental analysis reveals that **Form2** is partially dehydrated with the chemical formula of BCbpy·$2H_2O$. This result indicates that the lattice waters in the crystal not only play an important role in the wavelength-dependent luminescence behavior but also can be regarded as a switch between the single- and dual-color emissions (Fig.2e) The X-ray powder diffraction (XRPD) analysis demonstrates a reversible structural transformation during the dehydration and rehydration processes. As shown in Fig. 3, the phase purity of original samples is supported by a good match between the experimental XRPD pattern and the simulated one from the single-crystal structure. After grinding the sample at room temperature for 12 h, some diffraction peaks at the 2θ values of 16.74, 21.59 and 29.85° disappear, while new peaks at the 2θ values of 7.52, 11.02, 13.48, 20.99 and 24.65° appear, which indicates that a new crystalline phase emerges. Upon further grinding at 50 °C for additional 12 h, the diffraction peaks of the original sample at the 2θ values of 9.64, 11.87, 19.1, 22.87, 23.54 and 31.23 ° completely disappear, suggesting that **Form1** has been totally transformed into a new crystalline phase. This new crystalline phase (**Form2**) is stable at 50 °C. No change in the positions of diffraction peaks can be observed with increasing grinding time. After exposure of the dehydrated sample to moist atmosphere for 48 h, the XRPD pattern becomes identical to that of the original sample again, meaning that the dehydrated sample can reversibly revert to the original state via rehydration.

By dispersing **Form1** in the water-DMSO mixed solution and allowing slow evaporation, block crystals suitable for X-ray analysis can be obtained. XRPD analysis reveals that there is a good match between the simulated pattern from this single-crystal structure data and the experimental pattern of **Form2**. Thus, X-ray single crystal structural analysis can be carried out and clearly reveals that there is one BCbpy molecule in the asymmetric unit and no water aggregate exists in **Form2**. BCbpy molecules are linked by two lattice water molecules through O–H···O hydrogen bonds in a $R_4^2(8)$ type graph-set motif to form a dimer unit (Fig. S5, †ESI). The interplanar angle between the pyridine ring and the adjacent phenyl ring is 86.32°, which is slightly smaller than that observed in **Form1** (88.87°). Different from **Form1** in which two pyridine rings are twisted by 23.04° with respect to each other, the two pyridine rings in **Form2** are almost coplanar with a dihedral angle of 6.36°. Such a planar conformation leads to efficient π–π stacking interactions between bipyridine units, with the average interplanar distance of 3.49 Å (Fig. 4). Each hydrogen-bonded dimer unit is held together by this π–π stacking interaction into a close-packed layer. It is well known that the π–π stacking of the planar molecule may facilitate the formation of detrimental excimeric species and lead to fluorescence quenching in the solid state.[15] Therefore, the disappearance of the blue emission might be due to the quenching of the intrinsic fluorescence of bipyridinium chromophore by a close packed arrangement. The luminescence spectrum of **Form2** displays a main emission band at 574 nm, which is about 37 nm red shift from the low-energy emission of **Form1** (Fig. S6, †ESI). Such a bathochromic effect should be related to the conformational change of BCbpy molecule in different aggregation states.

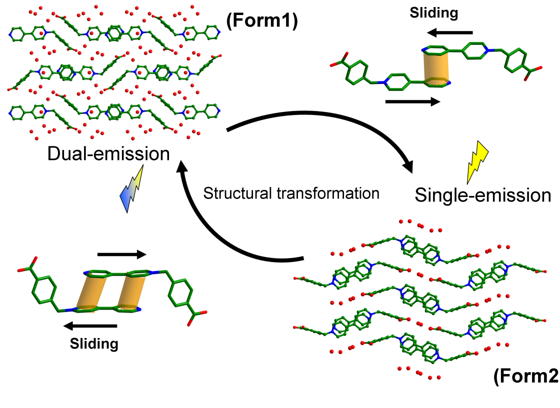

Fig. 4 Crystal packing mode for **Form1** (top) and **Form2** (bottom). Thick yellow lines represent π–π stacking interactions.

In summary, an interesting dual fluorescence emission has been detected in aqueous solution and the crystalline state for a carboxybenzyl-substituted bipyridinium zwitterion, and a reversible switching of luminescence between single and dual emissions by the variation in molecular stacking mode has also been achieved. The present work develops a kind of organic small molecule that emits single-color or almost-white light upon controlling excitation wavelength. The merit of easy synthesis and modification as well as tunable multicolour photoluminescence of this compound provide the inspiration for the design of new materials for labelling, sensing, color display and switching applications

This work was supported the NNSF of China (Nos. 20973171/20671090).

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