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A highly efficient solution and solid state ESIPT fluorophore and its OLEDs application

Virgile Trannoy, Anne Léaustic, Sophie Gadan, Régis Guillot, Clémence Allain, Gilles Clavier, Sandra Mazerat, Bernard Geoffroy* and Pei Yu*

We present herein the synthesis and the photophysics of 2,2'-bipyridine-3,3'-diol-5,5'-dicarboxylic acid ethyl ester (BP(OH)₂DCEt₂), an excited state intramolecular proton transfer (ESIPT)-based fluorophore featuring two identical intramolecular hydrogen bonds. BP(OH)₂DCEt₂ emits efficiently not only in solution, including protic solvents (λem = 521 nm, Φf = 40 to 75%), but also in crystalline state (λem = 530 nm, Φf = 51%). In addition, its saponified form (Na₂BP(OH)₂DC) is highly fluorescent in water (λem = 490 nm, Φf = 51%). Finally, the good electroluminescence performance of BP(OH)₂DCEt₂ is also demonstrated in an OLED device.

Introduction

Organic chromophores with intramolecular hydrogen bond are prone to undergo, upon light absorption, Excited-State Intramolecular Proton-Transfer (ESIPT), an ultrafast photochemical process that leads to a new excited state with an electronic structure quite different from the original one and gives rise thereby to a unique four-level photo-cycle, as illustrated in Scheme 1 in the case of an archetypal molecule of this family, 2-(2-hydroxyphenyl)-benzothiazole (HBT).

As a result, ESIPT chromophores display remarkable fluorescent features, with either a low energy K* emission or a dual and tunable E* and K* emission.1-4 Moreover, unlike most organic fluorophores they also tend to be highly fluorescent in water (Φf = 40 to 75%), but also in crystalline state (Φf = 51%). In addition, its saponified form (Na₂BP(OH)₂DC) is highly fluorescent in water (Φf = 51%). Finally, the good electroluminescence performance of BP(OH)₂DCEt₂ is also demonstrated in an OLED device.

Scheme 1. Four-level photocycle of HBT

Moreover, unlike most organic fluorophores they also tend to be highly fluorescent in water (Φf = 40 to 75%), but also in crystalline state (Φf = 51%). In addition, its saponified form (Na₂BP(OH)₂DC) is highly fluorescent in water (Φf = 51%). Finally, the good electroluminescence performance of BP(OH)₂DCEt₂ is also demonstrated in an OLED device.

The target linker derives from 2,2′-bipyridine-3,3′-diol (BP(OH)$_2$, Scheme 2), a molecule featuring two intramolecular hydrogen bonds and well-documented for its intense double-proton-transfer based fluorescence and applications.$^{24-32}$ More importantly, even in protic solvents such as MeOH and EtOH, where most ESIPT dyes are not or only weakly fluorescent, BP(OH)$_2$ keeps a more than decent quantum yield of 10 and 18%, respectively.$^{26}$ However, to our surprise, very few fluorescent derivatives of BP(OH)$_2$ have been reported in the literature.$^{33-38}$ In this work, we report the synthesis, crystal structure and photophysics of a highly fluorescent and functionalized BP(OH)$_2$ derivative, namely 2,2′-bipyridine-3,3′-diol-5,5′-dicarboxylic acid ethyl ester (BP(OH)$_2$DCEt$_2$, Scheme 2), precursor of H$_2$BP(OH)$_2$DC. The new compound substantially outperforms the parent BP(OH)$_2$ in solution, including in protic solvents, and emits efficiently in crystalline state. Finally, good electroluminescence performance of BP(OH)$_2$DCEt$_2$ is also demonstrated in an OLEDs device.

Results and discussion

Synthesis and characterizations

Starting from the commercially available 5-hydroxy-3-pyridinecarboxylate BP(OH)$_2$DCEt$_2$ was synthesized according to Scheme 3 in three straightforward steps with good overall yield.

Adapting a phosphine-free nickel catalytic system reported for the synthesis of symmetric and dissymmetric bipyridines,$^{39}$ 5-hydroxy-6-iodo-niconic acid ethyl ester was reductively homocoupled to give BP(OH)$_2$DCEt$_2$ in good yield. BP(OH)$_2$DCEt$_2$ was fully characterized by standard techniques as well as by single crystal analyses (more details can be found in the ESI). The molecule crystallizes in C2/c space group, with its molecular structure shown in Figure 1.

Figure 1. Molecular structure of BP(OH)$_2$DCEt$_2$ (top); π stacking (middle); angle between the long axis of two adjacent stacked molecules (bottom).

Like the parent BP(OH)$_2$ and its 6,6′-dimethyl substituted derivative,$^{40,41}$ BP(OH)$_2$DCEt$_2$ adopts a planar geometry due to the two strong and identical hydrogen bonds between the two pyridinic rings of the central BP(OH)$_2$ moiety (Figure 1, top). On the other hand, there is no intermolecular hydrogen bonding nor other close contacts between adjacent molecules except a significant π stacking that runs along the [101] crystallographic direction, with a mean interlayer distance of ca. 3.25 Å (Figure 1, middle). Note that the two adjacent molecules are not co-facial but more in a slip-stacking mode with, moreover, an angle of 48° between the long axis of the molecules (Figure 1, bottom).

Fluorescence

IN ORGANIC SOLVENTS. The emission properties of BP(OH)$_2$DCEt$_2$ were investigated by steady-state fluorescence at room temperature in four different and aerated solvents. Its
absorption and emission spectra are shown in Figure 2 and the main spectroscopic data listed in Table 1 along with available data of BP(OH)$_2$ for comparison.

![Normalized absorption and emission spectra of BP(OH)$_2$DCEt$_2$ in different solvents.](image)

**Figure 2.** Normalized absorption and emission spectra of BP(OH)$_2$DCEt$_2$ in different solvents.

<table>
<thead>
<tr>
<th>Solv.</th>
<th>$\lambda_{ab}$ (nm)</th>
<th>$\epsilon$ (M$^{-1}$ cm$^{-1}$)</th>
<th>$\lambda_{em}$ (nm)</th>
<th>$\Phi_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BP(OH)$_2$DCEt$_2$</td>
<td>C$<em>6$H$</em>{12}$</td>
<td>372, 389</td>
<td>521</td>
<td>0.70</td>
</tr>
<tr>
<td></td>
<td>CH$_2$Cl$_2$</td>
<td>372, 388</td>
<td>15900</td>
<td>521</td>
</tr>
<tr>
<td></td>
<td>MeCN</td>
<td>370, 375</td>
<td>521</td>
<td>0.57</td>
</tr>
<tr>
<td></td>
<td>MeOH</td>
<td>370, 385</td>
<td>521</td>
<td>0.40</td>
</tr>
<tr>
<td></td>
<td>H$_2$O+dmso(3%)</td>
<td>370, 385</td>
<td>540</td>
<td>0.29</td>
</tr>
<tr>
<td>BP(OH)$_2$</td>
<td>C$<em>6$H$</em>{12}$</td>
<td>340-350</td>
<td>500</td>
<td>0.31$^b$</td>
</tr>
<tr>
<td></td>
<td>CH$_2$Cl$_2$</td>
<td>340-350</td>
<td>500</td>
<td>0.21$^b$</td>
</tr>
<tr>
<td></td>
<td>MeCN</td>
<td>340-350</td>
<td>500</td>
<td>0.09$^a$</td>
</tr>
<tr>
<td></td>
<td>MeOH</td>
<td>340-350</td>
<td>480</td>
<td>0.10$^b$</td>
</tr>
<tr>
<td></td>
<td>H$_2$O</td>
<td>347, 403, 430</td>
<td>460</td>
<td>0.04$^a$</td>
</tr>
<tr>
<td>Na$_2$BP(OH)$_2$DC</td>
<td>H$_2$O</td>
<td>360, 426</td>
<td>490</td>
<td>0.51</td>
</tr>
</tbody>
</table>

$^a$ Ref. 24; $^b$ Ref. 27; $^c$ Ref. 26

BP(OH)$_2$DCEt$_2$ mainly absorbs in the UV region, with a strong and rather structured low energy band located between 370-385 nm, while its emission is broad and centred at 521 nm. Both the absorption and emission spectra only slightly vary with solvents of different polarity and proticity.

In comparison with BP(OH)$_2$, the major difference in absorption is a redshift of ca. 30 nm for the low energy band likely due to a more stabilized LUMO by the electron-withdrawing ester groups, while its emission is red-shifted by ca. 20 nm in aprotic solvents and ca. 40 nm in protic solvents like MeOH (Table 1). However, the most remarkable difference between the two is the quantum yield of emission. The new emitter has a much higher efficiency in all solvents investigated (Table 1). Particularly noteworthy is the still high quantum yield of 40% in methanol, which is four times that reported for BP(OH)$_2$. The emission was also studied by time-resolved fluorescence emission in dichloromethane. A single-exponential decay was observed with a fluorescence lifetime of 4.64 ns, which is superior to that of 3.2 ns reported for BP(OH)$_2$ in the same solvent. This emission is not sensitive to oxygen as the same decay was obtained in degassed dichloromethane.

The reasons to such an enhancement in the fluorescence efficiency are not yet clear. Due to the presence of electron-accepting ester group one could expect significant changes in the strength of the intramolecular hydrogen bond, which directly affects the ESIPT process and its emission. Actually, the measured chemical shift of the hydrogen atom engaged in the hydrogen bond ($\delta=14.40$ ppm) is very close to that reported for BP(OH)$_2$ ($\delta=14.54$ ppm), indicating therefore a very similar strength of the intramolecular hydrogen bonds within the two fluorophores. This unusually small substitution effect is however not unexpected since the enhancement of the hydrogen donating ability of the hydroxyl group is offset at least in part by a concomitant decrease in the hydrogen accepting capability of the nitrogen atom located on the same ring, leading thus to an overall limited impact on the hydrogen bonding in symmetrically substituted BP(OH)$_2$ derivatives.

One possible explanation to the observed fluorescence enhancement could be a better “insulation” of the emitting state from the solvent in BP(OH)$_2$DCEt$_2$ than in BP(OH)$_2$. This is best reflected in methanol where a blue shift in emission, observed for BP(OH)$_2$ (Table 1), is thought to be related to some specific interactions of its excited state (DK*, Scheme 2) through formation of intermolecular hydrogen bonds with protic solvents, while this is not the case for BP(OH)$_2$DCEt$_2$ (Table 1) probably due to a different pattern of intermolecular interactions between BP(OH)$_2$DCEt$_2$ and solvent molecules.

IN WATER. ESIPT dyes are generally not or only weakly fluorescent in water as the intramolecular hydrogen bond of the dye, mandatory for the ESIPT process, is disrupted or at least weakened to a large extent by formation of intermolecular hydrogen bonds. The high quantum yield of BP(OH)$_2$DCEt$_2$ in methanol suggests a better ESIPT emitter in water than the weakly fluorescent BP(OH)$_2$. The BP(OH)$_2$DCEt$_2$ being insoluble in water, dimethyl sulfoxide (DMSO) was used as co-solvent (3% in volume) to prepare an aqueous solution of the dye for fluorescence characterizations. To our delight, the solution remains highly fluorescent, with a slightly redshifted maximum at 540 nm and a measured quantum yield still up to 29% (Table 1). In addition, even if it is expected for ESIPT dyes, the high quantum yield makes the new emitter potential candidate as a sensitive pH probe. As a matter of fact, the fluorescence underwent drastic changes when the pH was gradually brought from 6 to 12 (Figure S1), while the emission colour changed from yellow-green to blue-cyan. Such changes are clearly associated with a progressive deprotonation of the two OH functions of BP(OH)$_2$DCEt$_2$. Using global analysis (ReactLab™-EQUILIBRIA) the fluorescence responses could be satisfactorily fitted with two proton dissociation constants of pKa = 8.1 and 11.3, respectively. These pKa values are smaller than those (9.2, 12.4) reported for BP(OH)$_2$, but consistent with the expected electron-withdrawing effect of ethyl ester group.

The dicarboxylic acid form of the new emitter, H$_2$BP(OH)$_2$DC (Scheme 2), is not sufficiently soluble in water for fluorescence measurements. This very low solubility can probably be attributed to the presence of multiple strong...
intermolecular hydrogen bonds between neighbouring molecules in the solid state. However, its disodium dicarboxylate form (Na₂BP(OH)₂DC, Scheme 2) is pretty soluble in water owing to its twice negatively charged nature at neutral pH. Its absorption and emission spectra are shown in Figure 3.

![Figure 3. Absorption and emission spectrum of Na₂BP(OH)₂DC in water (6 × 10⁻³ M) at 25°C.](image)

The absorption spectrum of Na₂BP(OH)₂DC in water is characterized by an intense band at 360 nm and two others of much lower intensity located between 400 and 480 nm (Table 1). This spectrum resembles qualitatively that of BP(OH)₂ in water and by analogy, the two bands at lower energy can be reasonably assigned to the zwitterionic diketo form stabilized in the ground state by formation of intermolecular hydrogen bonds with water molecules.

The emission of Na₂BP(OH)₂DC peaks at 490 nm and represents a redshift of ca. 30 nm in comparison with that of BP(OH)₂ (Table 1). But the most remarkable feature of this ESIPT emission is its quantum yield of 51%, which is more than ten times that of BP(OH)₂ in water.

Like BP(OH)₂DCEt₂, the fluorescence of Na₂BP(OH)₂DC is particularly sensitive to the pH of the solution, as shown in Figure 4.

![Figure 4. Fluorescence changes of Na₂BP(OH)₂DC versus pH in water at 25°C.](image)

In the pH range between 7 and 10, the observed changes in fluorescence are linked to the progressive deprotonation of the two OH functions and suggest the generation of a new blue emitting species, corresponding probably to the triple negatively charged species after first proton removal. While the rapid decrease in intensity of the initial fluorescence when lowering pH below 5 is likely due to the combination of two effects: 1) partial breakdown of the intramolecular hydrogen-bonds; 2) the formation of the scarcely water-soluble dicarboxylic form, H₂BP(OH)₂DC. Finally, analysis of the fluorescence response vs pH in the range from 5 to 10 allowed to determine the first proton dissociation constant (pKa) of the two OH functions to be 8.0, similar to what is obtained for the ester derivative BP(OH)₂DCEt₂.

**IN CRISTALLINE STATE.** The emission of BP(OH)₂DCEt₂ in solid state was investigated at room temperature by both steady-state fluorescence spectroscopy with an integrating sphere and time-resolved fluorescence.

The emission spectrum of the pristine microcrystals is qualitatively very close to that in solution, with a maximum centred around 530 nm and a measured quantum yield of 51% (Figure S2). Then the decay was monitored by time-resolved fluorescence at three different wavelengths of the emission: 510 nm (blue-edge), 530 nm (maximum) and 580 nm (red-edge). The three decays could be well fitted using a two-exponential model with decay times of 2.06 ns and 4.74 ns. The long decay time, making up to ca. 95% of the total fluorescence, is very close to the fluorescence lifetime measured in dichloromethane (4.64 ns), while the short decay (ca. 5%) could likely be ascribed to the surface and near-surface molecules in the microcrystals which experience a different environment. Comparison of the decays at different emission wavelengths shows that the relative contributions of the two decay times to the overall fluorescence only slightly vary with the emission wavelength, which indicate that there are no excited-state processes such as excimers or resonance energy transfer occurring in the solid.

The high solid-state quantum yield, comparable to those in solution, is clearly due to the absence of the so called “Aggregation Caused Quenching” (ACQ), generally encountered in solid state for organic dyes. Two reasons can be put forward. Firstly, resonance energy transfer, one of the main contributors to ACQ, is suppressed due to the absence of spectral overlap between the absorption and emission of the dye. Secondly, the crystal structure has favourable intermolecular arrangements (Figure 1). Indeed, the only significant intermolecular interactions are between molecules involved in a kind of π slip-stacking, which is believed to enhance solid state emission.

**Electroluminescence**

The electroluminescence properties of BP(OH)₂DCEt₂ were investigated to access its potential as emitting dye in OLEDs device whose structure is shown in Scheme 4. The emitting layer (EML) is BP(OH)₂DCEt₂ molecules either as neat film or host-guest system of 20 nm thick (See experimental for details of OLED fabrication and characterization).
Scheme 4. OLED device structure and molecular materials used.

The solid-state photoluminescence yields (PL) of the emitting layer are given in Table 2 and the PL spectrum is shown in Figure 5 for a 70 nm thick neat film. The PL emission peak is centred at 536 nm with a FWHM around 60 nm. The PL yields of the neat films are very high (~80 %) showing the interest of BP(OH)$_2$DCEt$_2$ molecule for OLEDs fabrication. For the guest-host films, the PL yield increases with the concentration of the BP(OH)$_2$DCEt$_2$ molecule in the host and particularly with mCP as host material. For 10% doping ratio, PL efficiency is higher for mCP than for DPVBi used as host. This could be explained by self-absorption or the particular morphology of the film as discussed below.

Table 2. Thin film PL efficiency

<table>
<thead>
<tr>
<th>Host</th>
<th>Doping ratio (%)</th>
<th>Film thickness (nm)</th>
<th>PL yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>no</td>
<td>100</td>
<td>20</td>
<td>77</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>70</td>
<td>85</td>
</tr>
<tr>
<td>mCP</td>
<td>1.5</td>
<td>20</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>20</td>
<td>54</td>
</tr>
<tr>
<td>DPVBi</td>
<td>0.7</td>
<td>20</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>20</td>
<td>31</td>
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<td></td>
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<td>20</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>20</td>
<td>32</td>
</tr>
</tbody>
</table>

*PL measurement accuracy is 10%*

![Figure 5. PL spectrum of a neat film of 70 nm thick (excitation at 405 nm)](image)

The electroluminescence (EL) performance of the OLED devices are reported in Table 3 for the neat film and for the guest-host systems as a function of the host material and the doping ratio and the EL spectra are shown in Figure 6.

Table 3. OLEDs devices performances.

<table>
<thead>
<tr>
<th>Host</th>
<th>Doping ratio (%)</th>
<th>EQE (%)</th>
<th>cd/A</th>
<th>Im/W</th>
<th>EL peak (nm)</th>
<th>Luminance (cd/m$^2$)</th>
<th>CIE chromaticity (x,y)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>mCP</td>
<td>1.5</td>
<td>1.4</td>
<td>5.3</td>
<td>1.7</td>
<td>540</td>
<td>1422</td>
<td>0.336; 0.592</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>1.5</td>
<td>5.1</td>
<td>1.7</td>
<td>540</td>
<td>1515</td>
<td>0.346; 0.600</td>
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<tr>
<td></td>
<td>10</td>
<td>1.5</td>
<td>5.3</td>
<td>1.7</td>
<td>540</td>
<td>1510</td>
<td>0.347; 0.600</td>
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<tr>
<td>DPVBi</td>
<td>0.7</td>
<td>1.7</td>
<td>5.4</td>
<td>1.6</td>
<td>532</td>
<td>1571</td>
<td>0.304; 0.554</td>
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<tr>
<td></td>
<td>1.4</td>
<td>2.3</td>
<td>7.5</td>
<td>2.6</td>
<td>536</td>
<td>2206</td>
<td>0.325; 0.569</td>
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<tr>
<td></td>
<td>1.8</td>
<td>2.2</td>
<td>7.2</td>
<td>2.6</td>
<td>536</td>
<td>2104</td>
<td>0.318; 0.577</td>
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<tr>
<td></td>
<td>4</td>
<td>1.8</td>
<td>6.0</td>
<td>2.0</td>
<td>536</td>
<td>1819</td>
<td>0.335; 0.593</td>
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<td></td>
<td>5.6</td>
<td>1.3</td>
<td>4.6</td>
<td>1.2</td>
<td>540</td>
<td>1260</td>
<td>0.342; 0.588</td>
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<tr>
<td></td>
<td>8</td>
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<td>-</td>
<td>-</td>
<td>-</td>
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<td></td>
<td>10</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>-</td>
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</tr>
</tbody>
</table>

*a* recorded at 10 mA/cm$^2$, *b* recorded at 30 mA/cm$^2$, error bar ± 10 %, - not measurable.
The EL spectra are similar to the PL spectrum of the neat film (Figure 5) showing that the EL emission is due to BP(OH)_2DCEt molecule. For the neat film (100 % doping ratio), the devices show a short-circuit and therefore no light is emitted. This result is explained by the crystallization of BP(OH)_2DCEt molecules after evaporation, as revealed by AFM (Figure S3), and the diffusion of aluminum electrode through the layer. When mCP is used as host, the EL device characteristics are almost constant from a doping ratio of 1.5% to 10%. The external quantum efficiency (EQE), luminous efficiency (cd/A) and power efficiency (lm/W) are 1.5 ± 0.2 %, 5.3 ± 0.5 cd/A and 1.7 ± 0.2 lm/W respectively. As shown in Figure 6a, the EL emission is from BP(OH)_2DCEt molecule with a complete transfer from the host to the guest molecule. For the neat film (100 % doping ratio), the EL peak is at the same position as for the mCP host. Surprisingly, the EL emission stopped for a doping ratio of 8 % and 10 % and the devices are short-circuited similarly to the results reported previously for the neat emitting layer. When mCP is used as host, the CIE coordinates have almost reached the ones of 5.6 %, the EL peak is at the same position as for the mCP host and the CIE coordinates have almost reached the ones with mCP host. Surprisingly, the EL emission stopped for a doping ratio of 5.6 %, the EL peak is at the same position as for the mCP host and the CIE coordinates have almost reached the ones with mCP host. Interestingly, its dicarboxylate form fluoresces efficiently in crystalline state, it is found to be a robust ESIPT emitter in all solvents investigated, including protic ones, with fluorescence quantum yields exceeding by far those of BP(OH)_2. More interestingly, its dicarboxylate form fluoresces efficiently in pure water with a quantum yield up to 51 %, and this fluorescence is highly pH dependent. In crystalline state, it is also found to be an excellent ESIPT emitter and performs quite decently as a pure fluorescent emitter in an OLED device. Of course, its EQE is far below the state of the art, but it is found to be a robust ESIPT emitter in all solvents investigated, including protic ones, with fluorescence quantum yields exceeding by far those of BP(OH)_2. More interestingly, its dicarboxylate form fluoresces efficiently in pure water with a quantum yield up to 51 %. This journal is © The Royal Society of Chemistry 20xx

Conclusions

In summary, we have designed and fully characterized a new ESIPT emitter derived from the well-known BP(OH)_2. It is found to be a robust ESIPT emitter in all solvents investigated, including protic ones, with fluorescence quantum yields exceeding by far those of BP(OH)_2. More interestingly, its dicarboxylate form fluoresces efficiently in pure water with a quantum yield up to 51 %. This fluorescence is highly pH dependent. In crystalline state, it is also found to be an excellent ESIPT emitter and performs quite decently as a pure fluorescent emitter in an OLED device. Of course, its EQE is far below the state of the art, but recent studies show that much higher EQE could be achieved with ESIPT chromophores displaying TADF (Thermally Activated Delayed Fluorescence) properties. Finally, with two ester functions that can be easily further derivatized the new emitter constitutes an appealing and versatile entrance for the design of novel luminescent systems.

Experimental

General: Solvents and reagents are used as received unless otherwise stated. Elemental analyses were performed by Service de Microanalyse, ICSN, 91198, Gif sur Yvette,
France. Fluorescence spectra were recorded either on a
Fluoromax-4 or a Fluorolog spectrometer (Horiba Jobin
Yvon). Fluorescence quantum yield in solution were
determined using 9,10-diphenylanthracene in cyclohexane as
reference (Φ = 0.9). Absolute fluorescence quantum yields of
crystalline BP(OH)\(_2\)DCE\(_2\) were measured using a Quanta-
Phi integrating sphere (Horiba Jobin Yvon). Fluorescence
decay curves were obtained by the time-correlated single-
photon counting (TCSPC) method with a femto-second laser
excitation composed of a Titanium Sapphire laser (Tsunami,
Spectra-Physics) pumped by a doubled Nd:YVO\(_4\) laser
(Millennia Xs, Spectra-Physics). Light pulses at 800 nm from
the oscillator were selected by an acusto-optic crystal at a
repetition rate of 4 MHz, and then doubled at 400 nm by a
nonlinear crystal. Fluorescence photons were detected at 90°
through a monochromator and a polarizer at magic angle by
means of a Hamamatsu MCP3809U photomultiplier,
connected to a SPC-630 TCSPC module from Becker &
Hickl. The instrumental response function was recorded
before each decay measurement with a FWHM (full width at
half-maximum) of ~25 ps. The fluorescence data were
analyzed using the Global software package developed at the
Laboratory for Fluorescence Dynamics at the University of
California, Irvine, which includes reconvolution analysis and
global nonlinear least-squares minimization method. UV-Vis
absorption spectra were recorded on a Varian Cary 5000
spectrometer equipped with a temperature control unit.

Syntheses

The commercially available but quite expensive ethyl 5-
hydroxy-3-pyridinecarboxylate and ethyl 5-hydroxy-6-iodo-
3-pyridinecarboxylic acid can be readily prepared from the much
cheaper corresponding acid and used without
chromatographic purifications for the synthesis of
BP(OH)\(_2\)DCE\(_2\) as follows.

**Ethyl 5-hydroxy-3-pyridinecarboxylate**: to a mixture of 5-
hydroxy-3-pyridinecarboxylic acid (5.00 g, 36 mmol) in
absolute ethanol (100 ml) cooled at 0 °C was added dropwise
thionyl chloride (10.5 ml, 172 mmol). The mixture was left to
warm up to room temperature and refluxed overnight.
After removal of the solvent under reduced pressure the residue was
dissolved in water (100 ml) and pH of the solution was
adjusted to 7 by cautious addition of solid sodium
bicarbonate in small portions. After filtration, washing
with water the title compound was obtained as an off-white
microcrystalline solid and used for the next step without
further purification (5.0 g, 83% yield). \(^1\)H NMR (CDCl\(_3\), 7.26
ppm): δ = 8.77 (s, 1H), 8.46 (s, 1H), 7.90 (s, 1H), 4.41 (q, \(J = 7.3\) Hz, 2H) and 1.41 (t, \(J = 7.3\) Hz, 3H).

**Ethyl 5-hydroxy-6-iodo-3-pyridinecarboxylate**: ethyl 5-
hydroxy-3-pyridinecarboxylate (5.00 g, 30 mmol), sodium
carbonate (6.36 g, 60 mmol) and iodine (7.61 g, 30 mmol) in
water (200 ml) were stirred vigorously at room temperature
overnight. The pH of the orange solution was then adjusted to
ca 7 with hydrochloric acid (1M) and the resulting beige
microcrystalline precipitate was filtered, washed with water
and dried under vacuum, affording the title compound (7.30
g, 83% yield). \(^1\)H NMR (CDCl\(_3\)): δ = 8.76 (d, \(J = 8.5\) Hz,
1H), 7.75 (d, \(J = 1.9\) Hz, 1H), 5.87 (bs, 1H), 4.40 (q, \(J = 7.0\)
Hz, 2H) and 1.40 (t, \(J = 7.0\) Hz, 3H).

**BP(OH)\(_2\)DCE\(_2\)**: ethyl 5-hydroxy-6-iodo-3-
pyridinecarboxylate (2.93 g, 10 mmol), LiCl (0.43 g, 10
mmol) and NiCl\(_2\).6H\(_2\)O (0.24 g, 1.0 mmol) were dissolved in
DMF (20 ml). To the resulting blue solution was added zinc
(0.78 g, 12 mmol) and the mixture was stirred at room
temperature under argon. After few minutes the mixture
turned deep red with concomitant rise of temperature to 40-
50 °C. Once subsided, the stirring continued for 1h at RT
and 1h at 50-55 °C to ensure the completion of the reaction. The
cooled mixture was made acidic (\(pH = 1\) to 2) with aqueous
HCl (~1M) and the mixture vigorously stirred 30 min. before
the pH was brought back to ca. 4 with solid NaHCO\(_3\)
and the mixture vigorously stirred 30 min. before the
aqueous phase was extracted with CH\(_2\)Cl\(_2\) (3x30 ml) and the
combined organic phase was dried over Na\(_2\)SO\(_4\) and
concentrated. The residue was subjected to column
chromatography (silica gel, CH\(_2\)Cl\(_2\) to afford the title
compound as brilliant yellow microcrystalline solid (1.215 g,
73%). \(^1\)H NMR (CDCl\(_3\)): δ = 14.40 (s, 2H), 8.70 (d, \(J = 1.8\)
Hz, 2H), 8.03, \(J = 1.8\) Hz, 2H), 4.44 (q, \(J = 7.0\) Hz, 4H), 1.42
(t, \(J = 7.0\) Hz, 6H). \(^1^C\) NMR (CDCl\(_3\), 77 ppm): 164.3, 156.2,
141.7, 137.6, 128.1, 127.0, 61.8, 14.3. HRMS (ESI):
C\(_{16}\)H\(_{14}\)N\(_2\)O\(_6\) found: 331.0931[M-H]; calculated: 331.0936.
Elemental analysis calculated (%) for C\(_{16}\)H\(_{14}\)N\(_2\)O\(_6\):
C 57.83, H 4.16, N 8.36. Copper II phthalocyanine (CuPc) is
grown by slow evaporation of BP(OH)\(_2\)DCE\(_2\) in a mixture of
CH\(_2\)Cl\(_2\) and MeCN at room temperature.

**OLEDs device fabrication and characterization**

The OLED devices were fabricated onto indium tin oxide
(ITO) glass substrates purchased from Xin Yang Technology
(90 nm thick, sheet resistance of 15 Ω/□). Prior to organic
layer deposition, the ITO substrates were cleaned by
sonication in a detergent solution, rinsed twice in de-ionized
water and then in isopropanol solution and finally treated with
UV-ozone during 15 minutes. The OLEDs stack used in this
study is the following: Glass / ITO / CuPc (10 nm) /
N\(_2\)N\(_2\)-bis(1-naphthalenyl)- N,N\(_2\)-bis-phenyl-(1,1'-biphenyl)-4,4'-diamine
(aNPB) as hole transport layer (HTL), bathocuproine (BCP)
as hole blocking layer (HBL), tris-(8-hydroxyquinoline)aluminum (Alq\(_3\)) as electron transport
layer (ETL), lithium fluoride as electron injection layer (EIL)
and 100 nm of aluminum as the cathode, respectively. The
architecture of the device as well as the molecular structure
of the materials are shown in Scheme 4. The emitting layer
(EML) is BP(OH)\(_2\)DCE\(_2\) molecule either as a neat film or a
host-guest system of 20 nm thick. The material used as host
is 1,3-Bis(N-carbazolyl)benzene (mCP) and 4,4'-bis(2,2-
diphenylvinyl)-1,1’-biphenyl, (DPVBi). BP(OH)₂DCEt₂ is used as guest with a doping ratio of 0.7 to 10 % weight in the guest-host EML. All the organic materials were purchased from commercial companies except for the BP(OH)₂DCEt₂ molecule. Organic layers were sequentially deposited onto the ITO substrate at a rate of 0.2 nm/s under high vacuum (10⁻⁷ mbar). The doping rate was controlled by simultaneous co-evaporation of the host and the dopant. An in-situ quartz crystal was used to monitor the thickness of the layer depositions with an accuracy of 5%. The active area of the devices defined by the Al cathode was 0.3 cm². The organic layers and the LiF/Al cathode were deposited in a one-step process without breaking the vacuum.

After deposition, all the measurements were performed at room temperature and under ambient atmosphere with no further encapsulation of devices. The current–voltage–luminance (I–V–L) characteristics of the devices were measured with a regulated power supply (ACT100 Fontaine) combined with a multimeter (Keithley) and a 1 cm² area silicon calibrated photodiode (Hamamatsu). Electroluminescence (EL) spectra and chromaticity coordinates of the devices were recorded with a PR650 SpectraScan spectrophotometer, with a spectral resolution of 4 nm. Photoluminescence (PL) properties of the EML layer are obtained at room temperature with an integrating sphere (LabSphere) and illumination with a 405 nm laser diode. For PL measurements, the films were deposited on pre-cleaned glass substrates in the same deposition sequence as for the OLED devices.

Conflicts of interest
There are no conflicts to declare.

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