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Stacking the deck: Three organic compounds are diamagnetic in solution but paramagnetic in the solid state. These compounds also show stacking-induced NIR absorption and peculiar ferromagnetic-to-antiferromagnetic phase transition in the solid state.



#### **Magnetic Properties**

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Stacking-Induced Diamagnetic/Para-magnetic Conversion of Imidazo[1,2*a*]pyridin-2(3*H*)-one Derivatives: **Near-Infrared Absorption and Magnetic Properties in the Solid State** 

### Stacking-Induced Diamagnetic/Paramagnetic Conversion of Imidazo[1,2a]pyridin-2(3H)-one Derivatives: Near-Infrared Absorption and Magnetic Properties in the Solid State

### Guoping Yong,\* Xuerui Zhang, Yumei Zhao, and Wenlong She<sup>[a]</sup>

Abstract: Herein, we present three imidazo[1,2-a]pyridin-2(3*H*)-one derivatives that are diamagnetic in solution, but paramagnetic in the solid state, possibly owing to a stacking-induced formation of phenoxide-type radicals. Notably, a larger bathochromic shift of the absorption (even up to the near-infrared region) of these three compounds was observed in the solid state than in solution, which was attributable to the ordered columnar stacking arrangements or their single-electron character as radicals in the solid state. Interestingly, compared to that in solution, (E)-3-(pyridin-4'ylmethylene)imidazo[1,2-*a*]pyridine 2-(3H)-one displayed a largely red-shifted emission (centered at 660 nm, with tailing above 800 nm) in the solid state. A larger bathochromic shift (260 nm) of the emission is an indication of

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better order and tight stacking in the solid state, which is brought about by the rigid and polar acceptor. These three compounds also reveal different magnetic susceptibilities at 300 K, thus implying that they possess various columnar stacking structures. Most interestingly, these three radicals exhibit unusual ferromagnetic-to-antiferromagnetic phase transitions, which can be attributed to anisotropic contraction and non-uniform slippage of the columnar stacking chains.

#### Introduction

There is increasing interest in molecular stacking arrangements in the solid state because they play a very important role in endowing organic materials with various properties. In general, stacking arrangements in the solid state are governed by various secondary intermolecular interactions, such as  $\pi-\pi$  stacking, hydrogen bonding, C-H- $\pi$ , dipole-dipole, ion- $\pi$ , and lone-pair- $\pi$  interactions.<sup>[1-6]</sup> Thus, the fine-tuning of intermolecular interactions through rational molecular design is a promising approach for controlling the interesting properties of functional molecular solids. Among the various optoelectronic properties, fluorescence is considered to be the most-sensitive and -efficient method for monitoring the molecular stacking arrangement. In fact, the development of purely organic solid luminescent materials is a challenging issue, because many luminophores are highly emissive in dilute solutions but become weakly luminescent or even non-emissive in the condensed phase. However, a series of aggregation-induced fluorescent and phosphorescent emissions of purely organic molecules have been reported.<sup>[7,8]</sup> Moreover, many examples of luminescence color change related to molecular aggregation<sup>[9]</sup> and/or stacking<sup>[10]</sup> have also been reported. Very recently, we reported various phosphorescent colors, including the direct white-light phosphorescent emission of purely organic materials, which was induced by the stacking arrangement,<sup>[11]</sup> anion– $\pi$  interactions,<sup>[12]</sup> or complexation to  $\beta$ -cyclodextrin.<sup>[13]</sup> Notably, the  $\pi$ -stacking and supramolecular interactions provide adequate molecular arrangements or dipole changes, which probably also lead to red-shifted absorption, even into the near-infrared (NIR) region in the solid state.<sup>[14]</sup>

On the other hand, for a molecular material to exhibit bulk magnetic ordering, it must possess unpaired electrons and a magnetic exchange pathway, which often depends on the arrangement of the molecules in the solid state. It is clear that the stacking of molecules in the solid state is necessary for the successful design of molecular magnetic materials.<sup>[15]</sup> Therefore, to exploit any interesting and useful magnetic properties, the arrangement of the radical molecules in the solid state must be controlled, which remains a challenging issue. The solid-state structures and magnetic properties of thiazyl radicals have been a focus of recent research. The physical properties of these radicals are intimately linked to their solid-state structures and progress in the development of these radicals as molecular materials is strongly dependent upon the ability to control the structure at both the molecular and supramolecular levels. Thiazyl radicals exhibit strong intermolecular interactions in stacking structures,

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which lead to many interesting magnetic properties, such as magnetic ordering,<sup>[16]</sup> room-temperature magnetic bi-stability,<sup>[17]</sup> and photo-induced phase transition.<sup>[18]</sup> Such interesting properties make thiazyl radicals highly attractive as building blocks for molecule-based magnetic materials.<sup>[19]</sup> We have been interested in the magnetic properties of the 2,3'-biimidazo[1,2-*a*]pyridin-2'-one (Hbipo<sup>-+</sup>) radical and its derivatives. Their interesting magnetic properties are intimate-ly linked to their solid-state stacking structures and/or supra-molecular interactions.<sup>[20]</sup> For example, zwitterionic radical Hbipo<sup>-+</sup> salts adopt slipped columnar  $\pi$ -stacked chains. Such stacking structures result in a near-room-temperature ferro-magnetic-to-antiferromagnetic phase transition and a high long-range ferromagnetic ordering temperature.<sup>[20a]</sup>

To explore new purely organic phosphorescent materials, we recently designed and synthesized a new class of organic compounds, (E)-3-benzylideneimidazo[1,2-a]pyridin-2(3H)ones, which exhibited stacking-induced phosphorescent color changes.<sup>[11b]</sup> We found that these compounds also revealed a dramatic increase in phosphorescent quantum yield (almost 100-fold increase) accompanying the formation of effective molecular aggregates in the solid state.<sup>[11b]</sup> Herein, we report three imidazo[1,2-a]pyridin-2(3H)-one derivatives and investigate their absorption, photoluminescence, and magnetic properties in solution and in the solid state. Notably, larger bathochromic shifts of the absorption (even into the NIR region) and emission were observed in the solid state than in solution, owing to ordered columnar stacking arrangements in the solid state. To our surprise, three imidazo[1,2-a]pyridin-2(3H)-one derivatives are diamagnetic in solution at room temperature, whereas they are paramagnetic with interesting magnetic properties in the solid state, possibly owing to the stacking-induced formation of phenoxide-type radicals.

#### **Results and Discussion**

#### Synthesis and Crystal-Structure Description

As described in Scheme 1, the reaction between the hydrochloride salt of imidazo[1,2-a] pyridin-2(3*H*)-one and aromatic aldehydes afforded three imidazo[1,2-a]pyridin-2-





(3H)-one derivatives, (E)-3-benzylidene-imidazo[1,2-a]pyridin-2(3*H*)-one (1), (*E*)-3-(4'-hydroxy-benzylidene)imidazo-[1,2-a]pyridin-2(3*H*)-one (2),and (E)-3-(pyridin-4'ylmethylene)imidazo[1,2-a]pyridin-2(3H)-one (3), through aldol condensation reactions under mild conditions. Orange single crystals of compound 1 were obtained, which crystallized in the triclinic space group  $P\overline{1}$ . The molecular structure of compound 1 is shown in the Supporting Information, Figure S1. Interestingly, compound 1 exhibited a trans configuration. According to the mechanism of the Pschorr cyclisation, the condensation of imidazo [1,2-a] pyridin-2(3H)-one with benzaldehyde should lead to a cis configuration of the phenyl and pyridyl groups; however, the product was the trans compound. Abramovitch and Hey reported that (E)-3-(2'-nitrobenzylidene)imidazo[1,2-a]pyridin-2(3H)-one adopted the *trans* configuration.<sup>[21]</sup> They thought that it was likely that there was dipolar repulsion between the pyridine nitrogen atom and the electronegative nitro group, which led to the observed stereochemistry.

As solutions in DMF or  $H_2O$ , compounds 1–3 are diamagnetic (S=0) and EPR silent at room temperature, as judged from their normal NMR spectra (see the Supporting Information, Figures S2-S7). Most notably, the EPR-silent spectra were practically independent of solvent (DMF, DMSO, or H<sub>2</sub>O), concentration ( $\times 10^{-8} - \times 10^{-3}$  M), and temperature (126-298 K). However, these compounds exhibited narrow isotropic EPR signals with g values of about 2.000 (which are characteristic of organic radicals) in the solid state at room temperature (see the Supporting Information, Figure S8). Moreover, in comparison with its <sup>13</sup>C NMR spectrum in solution, more signals of the carbon atoms were missing in the solid-state <sup>13</sup>C NMR spectrum of compound **1** (Figure 1), owing to paramagnetic relaxation effects.<sup>[22]</sup> Such a remarkable change indicates that stacking induces the formation of paramagnetic phenoxide-type radicals in the solid state (see the Supporting Information, Scheme S1). We think that the stacking effects could stabilize the phenoxide-type radicals in the solid state; however, the dissolution effect might lead to destabilization of the radicals in solution.



Figure 1. Solution ( $[D_6]DMSO$ ) <sup>13</sup>C NMR spectra and solid-state <sup>13</sup>C-CP/ MAS NMR spectra of compound **1**.

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Figure 2. Columnar stacking of compound 1.

Compound 1 forms a 1D columnar stacking chain along the *b* axis, in which (*E*)-3-benzylideneimidazo[1,2-*a*] pyridin-2(3*H*)-one molecules adopt a slipped head-to-tail stacking mode, as shown in Figure 2. Although the stacking distance is outside the range for van der Waals interactions, there are four kinds of intermolecular close contacts between neighboring molecules (C1···C7' 3.336 Å, C6···C10' 3.369 Å, C7···C9' 3.391 Å, and C8···C8' 3.257 Å, shorter than van der Waals distances). The columnar chains are further assembled into a 2D supramolecular network through lateral intermolecular C14–H···N1' hydrogen bonds (3.155 Å) between neighboring columns (see the Supporting Information, Figure S9).

#### UV/Vis/NIR Absorption Spectra of Compounds 1-3

As shown in Figure 3a, the absorption bands of compounds 1-3 in DMF or H<sub>2</sub>O within the range 300-460 nm are attributed to  $\pi - \pi^*$  and  $n - \pi^*$  transitions of the aromatic segments; the additional weak absorption band at 550 nm for compound 2 and the strong absorption band at 510 nm for compound 3 are probably due to intramolecular charge transfer. As expected, the use of a stronger acceptor (pyridine) leads to a bathochromic shift of the maximum absorption peak for compound 3 in solution. Notably, in the solid state, compound 3 reveals one absorption band at 620 nm, owing to a stacking effect. Compounds 1-3 display another unusually photophysical phenomenon: In the solid state, their absorbance even occurs in the NIR region, from 1100 nm to beyond 2000 nm (Figure 3b). The NIR absorption bands of compounds 1-3 are probably related to the head-to-tail transition dipoles of the columnar  $\pi$  stacks (Figure 2) and the 2D supramolecular network (see the Supporting Information, Figure S9), which provide adequate molecular arrangements and dipole changes for the lowenergy absorptions.<sup>[14b]</sup> Therefore, the stacked conjugated  $\pi\, systems,^{[14c]}$  as observed in the crystal structure of compound 1 and, presumably, also in compounds 2 and 3, can contribute to enhanced exciton radiative relaxation and to a red-shifted absorption, even into the NIR region in the solid state with respect to the solution data. Moreover, the NIR absorption might also be attributed to their single-elec-



Figure 3. UV/Vis/NIR spectra of compounds 1-3 a) as  $\times 10^{-4}$  M solutions in DMF or H<sub>2</sub>O and b) in the solid state.

tron character in the solid state, because many organic radicals with conjugated systems are known to be deeply colored and act as NIR absorbers.<sup>[23]</sup>

#### Photoluminescence of Compounds 1-3

As previously reported, compound 1 exhibits similar emission peaks (about 568 nm) as a 10 µM solution in DMF and in the solid state.<sup>[11b]</sup> The photoluminescence spectrum of compound 2 at room temperature as a  $\times 10^{-4}$  M solution in DMF only displays very weak peaks with  $\lambda_{max} \approx 576$  nm (see the Supporting Information, Figure S10); however, compound 2 shows no or very low photoluminescence in the solid state because of aggregation-induced emission quenching.<sup>[24]</sup> The room-temperature PL spectra of compound 3 as a  $\times 10^{-4}$  M solution in H<sub>2</sub>O and in the solid state are shown in Figure 4. In solution, compound 3 exhibits an emission peak at 400 nm, whilst it reveals a largely red-shifted emission (centered at 660 nm, with tailing above 800 nm) in the solid state. A larger bathochromic shift (260 nm) in the PL spectrum is an indication of better order and tight stacking in the solid state, owing to the rigid and polar acceptor.<sup>[14d]</sup> Indeed, compound **3** reveals a strong diffraction peak at  $2\theta$  $\approx$ 7.05° (see the Supporting Information, Figure S11), thus indicating that it has more-ordered stacking, which contributes to the red-shifted emission. Unlike compounds 1 and 2, compound 3, which contains a stronger acceptor, is bathochromically shifted into the deep-red region; therefore, a NIR emission above 750 nm can be expected by the intro-

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Figure 4. Room-temperature PL spectra of compound **3** as a  $\times 10^{-4}$  M solution in H<sub>2</sub>O solution (excitation at 330 nm) and in the solid state (excitation at 425 nm).

duction of a very strong acceptor or ordered stacking. Accordingly, a stronger acceptor is thought to decrease the emitting energy level, thereby leading to emission wavelengths in the deep-red (even NIR) region. The solid-state quantum yields of compounds 1 and 3 are 1.3 and 0.9%, respectively, which are clearly higher than those in solution (about 0.016%). The highly aggregated quantum yields of compounds 1 and 3 are ascribed to the stacking effect, thus leading to enhanced quantum yields.

#### Magnetic Properties of Compounds 1-3 in the Solid State

Indeed, compound **1** is a quasi-1D chain in which radical molecules mainly adopt a head-to-tail dimer structure with shorter intermolecular close contacts (two C1…C7' 3.336 Å). Then, the dimers form a quasi-1D chain through multiple intermolecular close contacts between the dimers (Figure 2). As shown in Figure 5, variable-temperature SQUID meas-



Figure 5. Temperature dependence of  $\chi_M T$  (field-cooled) for compound 1.

urements (1 kOe, 400–4 K) on a microcrystalline sample of compound **1** show that  $\chi_{\rm M}T$  at 300 K is only 0.020 emu K mol<sup>-1</sup>, which is clearly lower than that expected for an S=1/2 paramagnet, thus demonstrating the existence of diamagnetic dimers, as observed in the crystal structure. Upon cool-

ing from 400 K, the  $\chi_{\rm M}T$  value increases to a maximum of 0.020 emuKmol<sup>-1</sup> at 325 K, thus indicating a weak ferromagnetic interaction at high temperatures, at which the  $\chi_{\rm M}T$  value remains almost constant (in the range 288–325 K). Then,  $\chi_{\rm M}T$  gradually decreases to zero at 4 K, thus indicating a weak antiferromagnetic interaction. The temperature dependence of the magnetic susceptibilities of compounds **2** and **3** was measured at 1 kOe in the range 4–400 K. The  $\chi_{\rm M}T$  values at 300 K were 0.345 and 0.266 emuKmol<sup>-1</sup> for compounds **2** and **3**, respectively (Figure 6), which were



Figure 6. Temperature dependence of  $\chi_M T$  (field-cooled) for compounds **2** and **3**.

close to the theoretical value of  $0.375 \text{ emu K mol}^{-1}$  for one isolated spin of the radical (S=1/2, g=2.00). On cooling from 400 K, the  $\chi_{\rm M}T$  value slightly increases to a maximum of  $0.386 \text{ emu K mol}^{-1}$  at 362 K for compound **2** and  $0.302 \text{ emu K mol}^{-1}$  at 375 K for compound **3** (Figure 6), thus indicating a weak ferromagnetic interaction at high temperatures for both compounds 2 and 3. Below these temperatures, the  $\chi_M T$  value gradually decreases to zero at 4 K for both compounds 2 and 3 (Figure 6), also indicating that they reveal weak antiferromagnetic interactions. Unlike compound 1, compounds 2 and 3 possess higher magnetic susceptibilities, thus implying that compounds 2 and 3 could adopt columnar stacking structures (with no or few dimers). Indeed, compounds 1-3 exhibit different powder X-ray diffraction (PXRD) patterns (see the Supporting Information, Figure S11), thus also demonstrating different stacking structures in the solid state.

The magnetic behaviors of compounds 1–3 can be divided into two main regions, namely, ferromagnetic interactions above 288, 362, and 375 K, respectively, and antiferromagnetic interactions below these temperatures, thus showing ferromagnetic-to-antiferromagnetic phase transitions, which can be demonstrated by the cooling and warming measurements of susceptibility. Compound 1 shows a divergence above 285 K (Figure 7); compound 2 exhibits a wide thermal hysteresis from 300 to 390 K (Figure 8); compound 3 reveals a wide divergence (from 251 to 390 K), with a cross-point at about 338 K (Figure 9). These peculiar magnetic behaviors can be interpreted as follows: In the high-temperature

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Figure 7. Temperature dependence of the magnetic susceptibility of compound  $\mathbf{1}$  upon cooling ( $\blacksquare$ ) and heating ( $\Box$ ).



Figure 8. Temperature dependence of magnetic susceptibility of compound **2** upon cooling ( $\blacksquare$ ) and heating ( $\square$ ).



Figure 9. Temperature dependence of magnetic susceptibility of compound **3** upon cooling  $(\blacksquare)$  and heating  $(\Box)$ .

region, radical arrangements within a quasi-1D or 1D stacking chain accidentally satisfy the conditions that are required for a ferromagnetic interaction, but, upon cooling, the anisotropic contraction and non-uniform slippage of the columnar stacking chain can more-probably trigger the spin transition into antiferromagnetic interactions.<sup>[20b,c,25]</sup>

#### Conclusions

In summary, three new organic compounds have been readily obtained that are diamagnetic in solution at room temperature, but paramagnetic in the solid state, possibly related to the stacking-induced formation of phenoxide-type radicals. These three compounds also reveal stacking-induced NIR absorption from 1100 to beyond 2000 nm. Interestingly, deep-red emission with tailing above 800 nm is also observed for compound **3**, which is attributable to  $\pi$ -stacking order in the solid state. In the solid state, compounds **1–3** exhibit a peculiar ferromagnetic-to-antiferromagnetic phase transition, which is ascribed to anisotropic contraction and non-uniform slippage of the columnar stacking structure upon cooling. The facile synthesis and very interesting photophysical and magnetic properties of these compounds demonstrate their potential as multifunctional molecular materials, such as promising deep-red-emissive and magnetic materials with NIR absorption.

#### **Experimental Section**

#### General

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All reagents were obtained from commercial suppliers and used without further purification.

#### Synthesis of (E)-3-Benzylideneimidazo[1,2-a]pyridin-2(3H)-one (1)

A mixture of the hydrochloride salt of imidazo[1,2-a]pyridin-2(3H)-one (1.72 g, 10 mmol) and benzaldehyde (1.06 g, 10 mmol) in acetic acid (50 mL) was heated at 125 °C for 2.5 h. After cooling to RT, the resulting orange solid was collected by filtration and washed with EtOH. The orange solid was immersed in a saturated aqueous solution of NaHCO3 until no bubbles were observed. Then, the solid was filtered off and washed with water and EtOH. Recrystallization of the orange solid from DMF afforded orange single crystals that were suitable for X-ray diffraction analysis. Yield: 1.59 g (7.16 mmol, 71.6 %);  $^{1}H$  NMR (400 MHz,  $[D_6]DMSO, 25^{\circ}C): \delta = 8.67$  (d, J = 6.8 Hz, 1 H), 8.48 (dd, J = 6.6 Hz, 3.0 Hz, 2H), 7.94 (s, 1H), 7.74 (ddd, J=8.6 Hz, 7.0 Hz, 1.3 Hz, 1H), 7.51 (dd, J=5.1 Hz, 1.9 Hz, 3H), 7.06 (d, J=8.9 Hz, 1H), 6.86 ppm (td, J= 6.9 Hz, 1.1 Hz, 1 H); <sup>13</sup>C NMR (101 MHz, [D<sub>6</sub>]DMSO, 25 °C): δ=172.82, 162.72, 141.56, 132.02, 131.87, 131.32, 129.80, 128.32, 127.86, 114.69, 111.34 ppm; IR (KBr pellet):  $\tilde{\nu}$ =3411 (w), 1710 (s), 1674 (s), 1490 (vs), 1485 (s), 1401 (vs), 1341 (m), 1257 (s), 1451 (m), 1176 (m), 1104 (m), 1044 (w), 891 (m), 771 (m), 687 (w), 639 (w), 558 (m), 498 cm<sup>-1</sup> (m): HRMS (EI): *m/z* calcd for C<sub>14</sub>H<sub>10</sub>N<sub>2</sub>O: 222.24 [*M*]<sup>+</sup>; found: 222.22.

#### Synthesis of (E)-3-(4'-Hydroxybenzylidene)imidazo[1,2-a]pyridin-2(3 H)one (2)

According to the same reaction conditions as for the synthesis of compound **1**, except for the replacement of benzaldehyde with 4-hydroxybenzaldehyde (1.22 g, 10 mmol), afforded compound **2** as an orange-red solid. Yield: 1.84 g (7.73 mmol, 77.3 %); <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>]DMSO, 25 °C):  $\delta = 10.40$  (s, 1 H), 8.64 (d, J = 6.9 Hz, 1 H), 8.51 (d, J = 8.8 Hz, 2 H), 7.85 (s, 1 H), 7.72–7.65 (m, 1 H), 7.04 (d, J = 8.9 Hz, 1 H), 6.89 (d, J = 8.8 Hz, 2 H), 6.83 ppm (td, J = 6.9 Hz, 1.0 Hz, 1 H); <sup>13</sup>C NMR (101 MHz, [D<sub>6</sub>]DMSO, 25 °C):  $\delta = 173.15$ , 161.46, 161.10, 140.29, 135.13, 129.45, 128.61, 123.56, 115.30, 114.41, 111.24 ppm; IR (KBr pellet):  $\bar{\nu} = 3435$  (w), 1626 (s), 1566 (s), 1485 (s), 1461 (s), 1389 (vs), 1365 (s), 1305 (s), 1269 (s), 1200 (s), 1164 (vs), 831 (m), 795 (m), 759 (m), 591 (m), 522 cm<sup>-1</sup> (w); HRMS (EI): m/z calcd for C<sub>14</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>: 238.24 [*M*]<sup>+</sup>; found: 238.20.

## Synthesis of (E)-3-(Pyridin-4'-ylmethylene)imidazo[1,2-a]pyridin-2(3 H)-one (3)

According to the same reaction conditions as for the synthesis of compound **1**, except for the replacement of benzaldehyde with 4-pyridine formaldehyde (1.07 g, 10 mmol), afforded compound **3** as a deep-green solid. Yield: 0.91 g (4.08 mmol, 40.8 %); <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O, 25 °C):  $\delta$ =8.91 (d, *J*=5.9 Hz, 2H), 8.27 (s, 1H), 7.99 (t, *J*=8.0 Hz, 2H), 7.69 (s,

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1 H), 7.57 (d, J=8.7 Hz, 2H), 7.21 ppm (s, 1H); <sup>13</sup>C NMR (101 MHz, D<sub>2</sub>O, 25 °C):  $\delta = 159.87$ , 146.47, 145.41, 142.40, 139.11, 131.28, 130.76, 128.62, 117.41, 110.27, 107.52 ppm; IR (KBr pellet):  $\tilde{\nu} = 3423$  (w), 1626 (s), 1485 (vs), 1413 (m), 1365 (m), 1293 (m), 1200 (m), 1128 (s), 936 (m), 831 (m), 795 (m), 747 (m), 687 (m), 579 (w), 510 (m), 438 cm<sup>-1</sup> (w); HRMS (EI): m/z calcd for  $C_{13}H_9N_3O$ : 223.27 [M]<sup>+</sup>; found: 224.08.

#### X-ray Structure Determination

The X-ray diffraction measurements for compound **1** were performed on a Gemini S Ultra CCD diffractometer (Oxford diffraction Ltd.) by using graphite-monochromated  $Cu_{K\alpha}$  radiation ( $\lambda$ =1.54184 Å). The structure was solved by using direct methods and refined by full-matrix leastsquares methods on  $F^2$  by using the SHELXS-97 and SHELXL-97 programs.<sup>[26]</sup> All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed at geometrically calculated positions and refined by riding on their parent atoms. The weighted *R* factor ( $R_w$ ) and all goodness-of-fits (S) are based on  $F^2$ ; the conventional *R* factor (*R*) is based on *F*.

CCDC 853989 (1) 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.

#### Other Physical Measurements

FTIR spectra were recorded on a Bruker EQUINOX55 FTIR spectrophotometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Bruker Avance 400 MHz NMR spectrometers in [D<sub>6</sub>]DMSO or D<sub>2</sub>O as the solvent with tetramethylsilane (TMS) as an internal standard. High-resolution mass spectroscopy (HRMS) was performed on a Micromass GCT-MS instrument with a time-of-flight (TOF) mass detector that was operating in electron impact (EI) mode. Solution (×10<sup>-4</sup> M in DMF or H<sub>2</sub>O) and solidstate UV/Vis/NIR absorption spectra were recorded at RT on a DUV-3700 UV/Vis/NIR spectrometer. Solution ( $\times 10^{-4} \, \text{m}$  in DMF or  $H_2 \text{O})$  and solid-state photoluminescence (PL) spectra were determined at RT on a Fluorolog-3-TAU fluorescence spectrophotometer. Solid-state quantum yields were also measured on a Fluorolog-3-TAU fluorescence spectrophotometer that was equipped with a BaSO<sub>4</sub>-coated integrating sphere. The solution-state quantum yields were measured at RT by using quinine sulfate ( $\Phi = 0.54$ ) as a reference. Corrections were performed owing to the change in solvent refractive indices.<sup>[27]</sup> Powder X-ray diffraction (PXRD) patterns were collected on a Philips X'pert PRO SUPER diffractometer that was operating with nickel-filtered  $Cu_{K\alpha}$  radiation ( $\lambda\!=$ 1.540598 Å). EPR spectra were recorded on a JES-FA 200 ESR spectrometer at the X-band. The temperature dependence of the magnetic susceptibilities was measured for the microcrystalline samples on a SQUID magnetosusceptometer (Quantum Design MPMS).

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- [1] B. Moulton, M. J. Zaworotko, Chem. Rev. 2001, 101, 1629–1658.
- [2] F. J. M. Hoeben, P. Jonkheijm, E. W. Meijer, A. P. H. J. Schenning, *Chem. Rev.* 2005, 105, 1491–1546.
- [3] X. Zhang, X. Zhang, K. Zou, C. S. Lee, S. T. Lee, J. Am. Chem. Soc. 2007, 129, 3527–3532.
- [4] M. Mascal, I. Yakovlev, E. B. Nikitin, J. C. Fettinger, Angew. Chem. 2007, 119, 8938–8940; Angew. Chem. Int. Ed. 2007, 46, 8782–8784.
- [5] V. Gorteau, G. Bollot, J. Mareda, A. Perez-Velasco, S. Matile, J. Am. Chem. Soc. 2006, 128, 14788–14789.
- [6] V. Gorteau, G. Bollot, J. Mareda, S. Matile, Org. Biomol. Chem. 2007, 5, 3000–3012.
- [7] a) J. D. Luo, Z. L. Xie, J. W. Y. Lam, L. Cheng, H. Y. Chen, C. F. Qiu, H. S. Kwok, X. W. Zhan, Y. Q. Liu, D. B. Zhu, B. Z. Tang,

Chem. Commun. 2001, 1740–1741; b) B. K. An, S. K. Kwon, S. D. Jung, S. Y. Park, J. Am. Chem. Soc. 2002, 124, 14410–14415; c) J. Chen, C. C. W. Law, J. W. Y. Lam, Y. Q. Dong, S. M. F. Lo, I. D. Williams, D. B. Zhu, B. Z. Tang, Chem. Mater. 2003, 15, 1535–1546; d) Z. Li, Y. Q. Dong, J. W. Y. Lam, J. X. Sun, A. J. Qin, M. Haëussler, Y. P. Dong, H. H. Y. Sung, I. D. Williams, H. S. Kwok, B. Z. Tang, Adv. Funct. Mater. 2009, 19, 905–917; e) Y. N. Hong, J. W. Y. Lam, B. Z. Tang, Chem. Commun. 2009, 4332–4353.

- [8] a) X. W. Z. Yuan, Y. Shen, H. Zhao, J. W. Y. Lam, L. Tang, P. Lu, C. L. Wang, Y. Liu, Z. M. Wang, Q. Zheng, J. Z. Sun, Y. G. Ma, B. Z. Tang, *J. Phys. Chem. C* **2010**, *114*, 6090–6099; b) O. Bolton, K. Lee, H.-J. Kim, K. Y. Lin, J. Kim, *Nat. Chem.* **2011**, *3*, 205–210.
- [9] a) A. Kishimura, T. Yamashita, K. Yamaguchi, T. Aida, *Nat. Mater.* 2005, *4*, 546–549; b) Y. Dong, J. W. Y. Lam, A. Qin, Z. Li, J. Sun, H. H. Y. Sung, I. D. Williams, B. Z. Tang, *Chem. Commun.* 2007, 40–42; c) S. Srinivasan, P. A. Babu, S. Mahesh, A. Ajayaghosh, *J. Am. Chem. Soc.* 2009, *131*, 15122–15131.
- [10] a) R. Davis, N. P. Rath, S. Das, Chem. Commun. 2004, 74–75; b) T. Mutai, H. Satou, K. Araki, Nat. Mater. 2005, 4, 685–687; c) H. Zhang, Z. Zhang, K. Ye, J. Zhang, Y. Wang, Adv. Mater. 2006, 18, 2369–2372; d) T. Mutai, H. Tomoda, T. Ohkawa, Y. Yabe, K. Araki, Angew. Chem. 2008, 120, 9664–9666; Angew. Chem. Int. Ed. 2008, 47, 9522–9524; e) Y. Zhao, H. Gao, Y. Fan, T. Zhou, Z. Su, Y. Liu, Y. Wang, Adv. Mater. 2009, 21, 3165–3169; f) E. Quartapelle Procopio, M. Mauro, M. Panigati, D. Donghi, P. Mercandelli, A. Sironi, G. D' Alfonso, L. D. Cola, J. Am. Chem. Soc. 2010, 132, 14397–14399.
- [11] a) G. P. Yong, Y. M. Zhang, W. L. She, Y. Z. Li, J. Mater. Chem.
   **2011**, 21, 18520–18522; b) G. P. Yong, W. L. She, Y. M. Zhang, Dyes Pigm. **2012**, 95, 161–167.
- [12] G. P. Yong, Y. M. Zhang, W. L. She, CrystEngComm 2012, 14, 3923– 3929.
- [13] a) G. P. Yong, B. Zhang, Y. M. Zhang, G. S. Li, J. Mater. Chem. 2012, 22, 13481–13483; b) G. P. Yong, X. R. Zhang, W. L. She, Dyes Pigm. 2013, 97, 65–70.
- [14] a) G. Qian, Z. Y. Wang, *Chem. Asian J.* 2010, *5*, 1006–1029; b) A. D'Aléo, D. Gachet, V. Heresanu, M. Giorgi, F. Fages, *Chem. Eur. J.* 2012, *18*, 12764–12772; c) W. Z. Yuan, Y. Gong, S. Chen, X. Y. Shen, J. W. Y. Lam, P. Lu, Y. Lu, Z. Wang, R. Hu, N. Xie, H. S. Kwok, Y. Zhang, J. Z. Sun, B. Z. Tang, *Chem. Mater.* 2012, *24*, 1518–1528; d) X. B. Du, J. Qi, Z. Q. Zhang, D. G. Ma, Z. Y. Wang, *Chem. Mater.* 2012, *24*, 2178–2185.
- [15] D. A. Haynes, CrystEngComm 2011, 13, 4793-4805.
- [16] a) A. J. Banister, N. Bricklebank, I. Lavender, J. M. Rawson, C. I. Gregory, B. K. Tanner, W. Clegg, M. R. J. Elsegood, F. Palacio, *Angew. Chem.* 1996, 108, 2648–2650; *Angew. Chem. Int. Ed. Engl.* 1996, 35, 2533–2535; b) A. Alberola, R. J. Less, C. M. Pask, J. M. Rawson, F. Palacio, P. Oliete, C. Paulsen, A. Yamaguchi, R. D. Farley, D. M. Murphy, *Angew. Chem.* 2003, 115, 4930–4933; *Angew. Chem. Int. Ed.* 2003, 42, 4782–4785.
- [17] a) W. Fujita, K. Awaga, *Science* 1999, 286, 261–262; b) W. Fujita, K. Awaga, H. Matsuzaki, H. Okamoto, *Phys. Rev. B* 2002, 65, 064434;
  c) J. L. Brusso, O. P. Clements, R. C. Haddon, M. E. Itkis, A. A. Leitch, R. T. Oakley, R. W. Reed, J. F. Richardson, *J. Am. Chem. Soc.* 2004, *126*, 8256–8265.
- [18] H. Matsuzaki, W. Fujita, K. Awaga, H. Okamoto, *Phys. Rev. Lett.* 2003, 91, 017403.
- [19] a) K. E. Preuss, *Dalton Trans.* 2007, 2357–2369; b) J. M. Rawson, A. Alberola, A. Whalley, *J. Mater. Chem.* 2006, *16*, 2560–2575; c) W. Fujita, K. Kikuchi, *Chem. Asian J.* 2009, *4*, 400–405; d) S. M. Winter, K. Cvrkalj, P. A. Dube, C. M. Robertson, M. R. Probert, J. A. K. Howard, R. T. Oakley, *Chem. Commun.* 2009, 7306–7308.
- [20] a) G. P. Yong, C. F. Li, Y. Z. Li, S. W. Luo, *Chem. Commun.* 2010, 46, 3194–3196; b) Y. Z. Li, G. P. Yong, Y. M. Zhang, C. F. Li, W. L. She, *Synth. Met.* 2011, 161, 713–717; c) Y. M. Zhang, G. P. Yong, C. F. Li, W. L. She, Y. Z. Li, *Synth. Met.* 2012, 161, 2708–2713; d) G. P. Yong, Y. M. Zhang, B. Zhang, *CrystEngComm* 2012, 14, 8620–8625; e) G. P. Yong, Y. M. Zhang, W. L. She, *Mater. Lett.* 2013, 92, 358–360.
- [21] R. A. Abramovitch, D. H. Hey, J. Chem. Soc. C 1966, 1095-1096.

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.....

- Fischer, E. Daltrozzo, A. Zumbusch, *Angew. Chem.* 2011, 123, 1442–1445; *Angew. Chem. Int. Ed.* 2011, 50, 1406–1409; d) G. Ulrich, S. Goeb, A. D. Nicola, P. Retailleau, R. Ziessel, *J. Org. Chem.* 2011, 76, 4489–4505.
- [25] X. M. Ren, S. Nishihara, T. Akutagawa, S. Noro, T. Nakamura, W. Fujita, K. Awaga, Z. P. Ni, J.-L. Xie, Q. J. Menge, R. K. Kremer, *Dalton Trans.* 2006, 1988–1994.
- [26] G. M. Sheldrick, SHELXL-97 and SHELXS-97, University of Göttingen, Göttingen, Germany, 1998.
- [27] C. F. Li, G. P. Yong, Y. Z. Li, Inorg. Chem. Commun. 2010, 13, 179– 182.

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- [22] R. Santo, R. Miyamoto, R. Tanaka, T. Nishioka, K. Sato, K. Toyota, M. Obata, S. Yano, I. Kinoshita, A. Ichimura, T. Takui, Angew. Chem. 2006, 118, 7773–7776; Angew. Chem. Int. Ed. 2006, 45, 7611– 7614.
- [23] a) J. Fabian, H. Nakazumi, M. Matsuoka, Chem. Rev. 1992, 92, 1197–1226; b) M. Kivala, C. Boudon, J.-P. Gisselbrecht, B. Enko, P. Seiler, I. B. Müller, N. Langer, P. D. Jarowski, G. Gescheidt, F. Diederich, Chem. Eur. J. 2009, 15, 4111–4123; c) D. Reitzenstein, T. Quast, F. Kanal, M. Kullmann, S. Ruetzel, M. S. Hammer, C. Deibel, V. Dyakonov, T. Brixner, C. Lambert, Chem. Mater. 2010, 22, 6641–6655; d) J. Chen, R. F. Winter, Chem. Eur. J. 2012, 18, 10733–10741.
- [24] a) S. W. Thomas, III., G. D. Joly, T. M. Swager, *Chem. Rev.* 2007, 107, 1339–1386; b) A. C. Grimsdale, K. L. Chan, R. E. Martin, P. G. Jokisz, A. B. Holmes, *Chem. Rev.* 2009, 109, 897–1091; c) G. M.

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