Highly luminous substituted bipyrroles

Chi-Ming Che,*[a] Chun-Wai Wan,[a] Wei-Zhu Lin,[a] Wing-Yiu Yu,[a] Zhong-Yuan Zhou,[b] W.-Y. Lai[c] and S.-T. Lee[c]

[a] *Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, China.*
E-mail: cmche@hku.hk
[b] *Open Laboratory of Chirotechnology, Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Hunghom, Hong Kong, China*
[c] *Centre of Super-Diamond and Advanced Film and Department of Physics and Materials Science, City University of Hong Kong, Tat Chee Avenue, Hong Kong, China*

Received (in Cambridge, UK) 4th December 2000, Accepted 27th February 2001
First published as an Advance Article on the web 29th March 2001

Two functionalized bipyrroles, 3,3′,5,5′-tetraethoxycarbonyl-4,4′-dipropyl-2,2′-bipyrrole 1 and 3,3′,5,5′-tetraethoxycarbonyl-4,4′-diphenyl-2,2′-bipyrrole 2, are highly luminescent materials at room conditions; they show UV emission at λ_{max} = 416 (1) and 414 nm (2) with quantum yields close to unity in the solid state; the molecular structure of 2 shows a coplanar structure stabilized by intramolecular hydrogen bonds, and the molecules are self-assembled along the crystallographic *c* axis by π-stacking interaction to form a one-dimensional chain; electroluminescence of 1 is evaluated.

The chemical, physical and electronic properties of conducting conjugated organic polymers such as poly(*p*-phenylenevinylenes)[1] and polythiophenes[2] have been widely exploited for the past decade, and recently some of these materials have been successfully developed for application in molecular electronics and light-emitting diode (LED) devices. However, among the numerous conducting polymers prepared to date, polypyrroles are the most extensively studied.[3] Apparently, polypyrroles possess a number of features that are attractive to materials science such as environmental stability, good redox properties and high electrical conductivity. Several applications based on polypyrroles including supercapacitors, electrochemical sensors, anti-static coating and drug delivery systems have been resulted.[4] Apart from these applications, to our knowledge, there are no reports describing highly luminescent poly/oligopyrroles at ambient conditions in the literature. Herein, we present the first report on UV photoluminescence of two functionalized bipyrrole compounds, namely 3,3′,5,5′-tetraethoxycarbonyl-4,4′-dipropyl-2,2′-bipyrrole **1** and 3,3′,5,5′-tetraethoxycarbonyl-4,4′-diphenyl-2,2′-bipyrrole **2** (Fig. 1). Blue luminous materials for application in blue-light emitting devices has recently been receiving widespread interest in materials science. We[5] and others[6] have reported that metal complexes of some *N*-heterocycles such as 7-azaindole, di-2-pyridylamine and 2,6-bis(2-pyridylamino)pyridine are strongly luminescent in the UV region; some of them have shown promising results as light-emitters for LED fabrication.[5b]

As reported by Nonell *et al.*,[7] **1** and **2** were prepared by the copper-mediated dehalogenated coupling of the iodopyrroles. The crude products were recrystallized by slow solvent evaporation of a CH_2Cl_2–MeOH mixture to afford colorless needle-shaped crystals.† As depicted in Fig. 2(a), the bipyrrole **2** adopts a near planar structure in a transcoid configuration, where the carbonyl functions of the carboxylate substituents are hydrogen bonded with the pyrrolic NH groups [N(1)···O(1A) 2.651 Å; N(1)···O(4) 2.486 Å]. It should be noted that the interannular torsion angle of unsubstituted 2,2′-bipyrrole for the most stable conformation is about 30° along the principal molecular axis according to theoretical models and some physical measurements.[8] In this work, we found that the coplanar conformation of **2** is essentially stabilized by intramolecular hydrogen bonding. Indeed, several studies by Brédas *et al.* have pointed out that coplanarity of the polyaromatic materials would permit better π-conjugation, thereby lowering the ionization potential and band gap of the compounds.[9] It is also suggested that coplanar conformation of polypyrroles

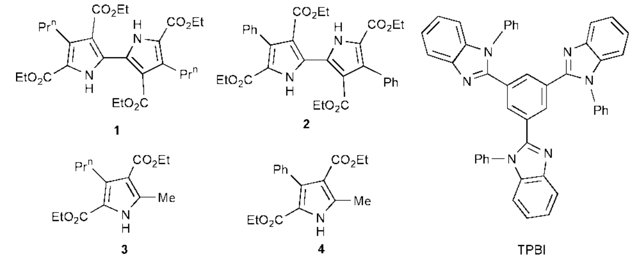
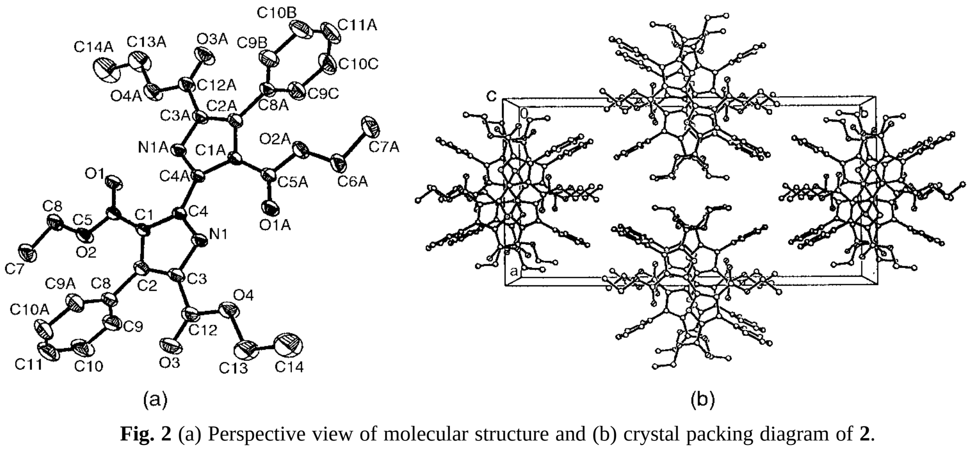


Fig. 1 Functionalized bipyrroles: 3,3′,5,5′-tetraethoxycarbonyl-4,4′-dipropyl-2,2′-bipyrrole **1** and 3,3′,5,5′-tetraethoxycarbonyl-4,4′-diphenyl-2,2′-bipyrrole **2**.



(a) (b)

Fig. 2 (a) Perspective view of molecular structure and (b) crystal packing diagram of **2**.

DOI: 10.1039/b009687n

Table 1 Photophysical data for bipyrroles **1** and **2**

	UV–VIS λ_{max}/ nm (ε/dm^3 mol^{-1} cm^{-1})[a]	Emission maxima λ_{max}/nm (298 K)			Lifetime[e]	
		Solid state	CH_2Cl_2	Φ_{em}[b]	Solid state	Solution[f]
1	250 (38020) 350 (30940)	416	415	0.56[c]	2.0	2.7
2	290 (21020) 346 (34950)	414, 431(sh)	401	0.87[c]	0.63, 3.39	0.3, 2.5
3	271 (16780)	—[d]	313	0.0016		
4	275 (16820)	—[d]	360	0.0175		

[a] In CH_2Cl_2 at 298 K. [b] In degassed CH_2Cl_2 [c] Excited at 345 nm. [d] Intensity too weak to measure. [e] Excited at 266 nm ps pulses (T = 300 K). [f] In degassed CH_2Cl_2 (1 mM).

could facilitate intrachain mobility of charge defects such as polarons or bipolarons.[9b,c] By comparing the absorption spectra with those of the mono-pyrrole analogues (2,4-diethoxycarbonyl-5-methyl-3-propylpyrrole **3** and 2,4-diethoxylcarbonyl-5-methyl-3-phenylpyrrole **4**),[10] the absorptions for the bipyrroles are significantly red-shifted (see Table 1) due to the extended π-conjugation of the molecules.

The phenyl rings are oriented perpendicular to the bipyrrole plane, and the four carboxylate groups are arranged in a spiral arrangement along the principal C_2 axis of the molecule. The respective O(1)–C(5) and O(3)–C(12) distances of 1.212(1) and 1.187(1) Å are consistent with a C=O formulation, and the C(1)–C(5) [1.457(1) Å], C(3)–C(12) [1.473(2) Å] and C(4)–C(4A) [1.462(2) Å] distances are slightly shorter than a typical C–C (sp^3-hybridized) single bond, suggesting the presence of a partial double bond character. The molecule appears to form a one-dimensional chain along the crystallographic *c* axis *via* intermolecular π-stacking interaction [see Fig. 2(b)], the interplanar separation is *ca.* 3.8 Å [N(1)–N(1′) 3.669 Å and C(1)–C(1′) 3.723 Å].

The absorption and emission data of the bipyrroles are shown in Table 1. Their absorption spectra are featured by two absorption bands (250 and 350 nm for **1**; 290 and 346 nm for **2**), presumably arisen from π–π* transitions. Importantly, both compounds are strongly luminous at around 400 nm. In CH_2Cl_2 solution, the emission quantum yields (Φ_{em}) of **1** and **2** are 0.56 and 0.87, respectively, and their solid state quantum yields are unity within the experimental error. We observed a large Stokes shift with a magnitude of *ca.* 4500 cm^{-1} for the emission from the lowest singlet π–π* transition of the bipyrroles, which suggests a significant structural distortion of the excited state from the ground state structure. For better understanding the nature of emission, we have examined the emission of the bipyrroles using picosecond laser spectrophotometer. The luminescent lifetimes are listed in Table 1. The short lifetimes suggest that the emissions are due to fluorescence arising from the singlet π–π* transitions. Upon cooling the solid sample of **1** to 15 K, a vibronically structured emission was identified with a peak splitting of *ca.* 1080 cm^{-1}, which corresponds to the skeletal vibration of the bipyrrole. The measured luminescence lifetime was found to be 5.9 ns.

The transient luminescence trace of **2** monitored at 420 nm revealed two decay processes with lifetimes being 0.63 and 3.39 ns in the solid state, and 0.3 and 2.5 ns in solution. For **1**, however, there is only a single exponential decay with lifetime being 2.0 and 2.7 ns in the solid state and CH_2Cl_2 solution, respectively. We propose that the short luminescence decay [*i.e.* lifetime = 0.3 ns (solution) and 0.63 ns (solid)] for **2** may have originated from the rapid excited state energy transfer between the bipyrrole ring(s) and the phenyl substituent(s).[11]

The electroluminescence (EL) of the bipyrrole **1** has been evaluated. A film of **1** (20 or 50 nm) was obtained by vapor deposition onto a glass substrate pre-coated with indium–tin oxide and 4,4′-bis[*N*-(1-naphthyl)-*N*-phenylamino)biphenyl (NPB; thickness = 80 nm). To achieve better contact between the emitter layer (*i.e.* **1**) and the Mg : Ag cathode, a layer of TPBI (40 or 20 nm, see Fig. 1 for structure) was evaporated on top of the bipyrrole layer. When the LED was forward biased with the ITO electrode at positive polarity, EL with a blue–green color was observed. The EL spectrum shows a prominent band at 440 nm, which is red–shifted from the solid state emission of **1** (blue color, λ_{max} = 415 nm). It should be noted that the PL spectrum of the bipyrrole film is essentially identical with the solid state emission of **1**. The reasons underlying the red-shift of the EL remain unclear. The maximum luminance of 750 cd m^{-2} with maximum efficiency being 0.9 cd A^{-1} was attained at 14 V.

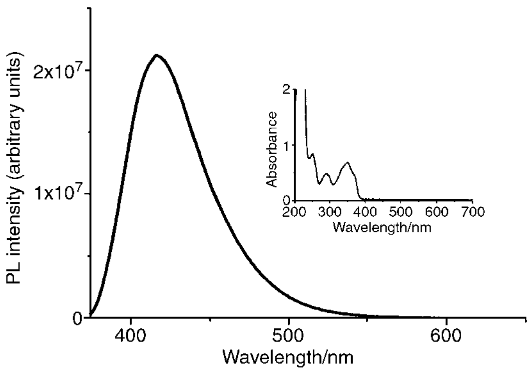


Fig. 3 Emission and absorption (inset) spectra of **1** in CH_2Cl_2 solution at 298 K.

We acknowledge the support from The University of Hong Kong and the Hong Kong Research Grants Council.

Notes and references

† *X-Ray crystallography*: the intensity data were collected on a Bruker CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at room temperature. All the calculations were performed by using SHELXTL-PL version 5.10 package on a HP computer. The structure was solved by the direct methods and refined by the full-matrix least-squares methods. *Crystal data* for **2**: colorless needle, dimensions 0.22 × 0.08 × 0.08 mm, $C_{32}H_{32}N_2O_8$, M_r = 572.60, orthorhombic, space group = *Ibam*, a = 14.363(2), b = 27.535(4), c = 7.272(1) Å, V = 2876.2(7) Å^3, Z = 4, D_c = 1.322 g cm^{-3}, F(000) = 1208; μ(Mo-Kα)/mm^{-1} = 0.577, 9113 reflections were collected, of which 1742 with $|F_o| > 2.0\sigma(|F_o|)$ were observed; R_1 = 0.054; wR_2 = 0.15. CCDC 156695. See http://www.rsc.org/suppdata/cc/b0/b009687n/ for crystallographic files in .cif format.

1 A. Kraft, A. C. Grimsdale and A. B. Holmes, *Angew. Chem., Int. Ed.*, 1998, **37**, 402 and references therein.

2 J. Roncali, *Chem. Rev.*, 1992, **92**, 711; G. Schopf and G. Kossmehl, *Adv. Polym. Sci.*, 1997, **129**, 1.

3 J. Simonet and J. R. Berthelot, *Prog. Solid State Chem.*, 1991, **21**, 1; D. L. Wise, G. E. Winek, D. J. Trantolo, T. M. Cooper and J. D. Gresser, in *Electrical and Optical Polymer Systems*, Marcel Dekker, Inc., New York, 1998, vol. 17.

4 B. Scrosati, *Applications of Electroactive Polymers*, Chapman & Hall, London, 1993; J. Rodriguez, H. J. Grande and T. F. Otero, in *Handbook of Organic Conductive Molecules and Polymers*, ed. H. S. Nalwa, John Wiley & Sons, New York, 1997, p. 415.

5 (*a*) C.-F. Lee, K.-F. Chin, S.-M. Peng and C.-M. Che, *J. Chem. Soc., Dalton Trans.*, 1993, 467; (*b*) Y. Ma, H.-Y. Chao, Y. Wu, S.-T. Lee, W.-Y. Yu and C.-M. Che, *Chem. Commun.*, 1998, 2491; (*c*) K.-Y. Ho, W.-Y. Yu, K.-K. Cheung and C.-M. Che, *Chem. Commun.*, 1998, 2101; (*d*) K.-Y. Ho, W.-Y. Yu, K.-K. Cheung and C.-M. Che, *J. Chem. Soc., Dalton Trans.*, 1999, 1581.

6 S.-F. Liu, Q. Wu, H. L. Schmider, H. Aziz, N.-X. Hu, Z. Popovic and S. Wang, *J. Am. Chem. Soc.*, 2000, **122**, 3671; W. Yang, H. Schmider, Q. Wu. Y.-S. Zhang and S. Wang, *Inorg. Chem.*, 2000, **39**, 2397.

7 S. Nonell, N. Bou, J. I. Borrell, J. Teixido, A. Villanueva, A. Juarranz and M. Canete, *Tetrahedron Lett.*, 1995, **36**, 3405.

8 C. Gatti, G. Frigerio, T. Benincori, E. Brenna, F. Sannicoló, G. Zotti, S. Zecchin and G. Schiavon, *Chem. Mater.*, 2000, **12**, 1490 and references therein.

9 (*a*) J. L. Brédas, R. Silbey, D. S. Boudreaux and R. R. Chance, *J. Am. Chem. Soc.*, 1983, **105**, 6555; (*b*) J. L. Brédas and G. B. Street, *Acc. Chem. Res.*, 1985, **18**, 309; (*c*) J. L. Brédas, G. B. Street, B. Themans and J. M. Andre, *J. Chem. Phys.*, 1985, **83**, 1323; (*d*) J. L. Brédas and A. J. Heeger, *Macromolecules*, 1990, **23**, 1150.

10 For preparation, see: A. C. Braithwaite and T. N. Waters, *J. Inorg. Nucl. Chem.*, 1973, **35**, 3223.

11 T. Sato, K. Hori, M. Fujitsuka, A. Watanabe, O. Ito and K. Tanaka, *J. Chem. Soc., Faraday Trans.*, 1998, **94**, 2355.