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New bichromophoric-2,2′-bipyridines: synthesis and optical properties

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Abstract—The synthesis and characterization of new unsymmetrically substituted bipyridyl-based chromophores featuring π-conjugated donor, acceptor or photoisomerizable backbones are reported. Their absorption and emission properties are discussed in comparison to those of the parent ligands.

2,2′-Bipyridines are ubiquitous chelating ligands in coordination chemistry, and the resulting metal complexes have been intensively studied for their chemical, electrochemical and optical properties.[1] Another interest is their uses as building blocks for the construction of efficient molecular and macromolecular nonlinear optical (NLO) chromophores.[2–5] During the last decade, our group has mainly been concerned with the NLO properties of octupolar tris(4,4′-π-donor substituted-2,2′-bipyridine) metal complexes in which intra-ligand charge transfer transitions (ILCT) mainly contribute to the NLO response.[6] In this respect, we have developed several methods for the preparation of symmetrical bipyridines featuring a variety of π-donor conjugated substituents such as *p*-dibutylaminostyryl (**1**)[7] and very recently the photoisomerizable *p*-dibutylaminophenylazostyryl group (**2**).[8] In order to design octupolar NLO-phores in which the NLO activity would be associated with only metal-to-ligand charge transfer transitions (MLCT), we also reported the synthesis of bipyridine **3** bearing the strong electron-accepting *p*-nitrostyryl substituent (Scheme 1).[7] Unfortunately, attempts to prepare the corresponding metal complexes were unsuccessful due to the very poor solubility of **3** in common organic solvents. Continuing our work toward chromophores based on functionalized bipyridyl ligands, we sought to prepare unsymmetrical bipyridines incorporating electron donor (**D**) and acceptor (**A**) moieties. With such type of 'push–pull' bichromophoric molecule, it might be possible to design a novel class of D_3 octupolar *fac*-tris(bipyridine) metal complexes with alternating **D** and **A** groups. In this Letter we report the synthesis and optical properties of the first example of such **D-bpy-A** chromophore (**4**), in which *p*-dibutylaminostyryl and *p*-nitrostyryl substituents are the donor and acceptor parts, respectively. By using the same strategy, we also describe the preparation of another interesting unsymmetrically disubstituted bipyridine (**5**) containing on one side a fluorophore and on the other side a photoisomerizable azobenzene group.

Scheme 2 depicts the synthetic pathways we used to prepare the key intermediate **9**. This compound was obtained in 64% overall yield by using a four-step synthesis. The first step involved the deprotonation of 4,4′-dimethyl-2,2′-bipyridine with 1 equiv of LDA followed by addition of *p*-dibutylaminobenzaldehyde, giving rise to **6** in quantitative yield. The trimethylsilyl derivative **7** was prepared by addition of another equivalent of LDA followed by trapping the resulting anion with TMSCl. The bromomethyl derivative **8** was then produced in high yield (92%) by using the procedure already described to prepare 4,4′-bis(bromomethyl)-2,2′-bipyridine.[9] Finally the phosphonate derivative **9** was synthesized in good yield (80%) by means of an Arbuzov reaction.[6,10]

Keywords: Bipyridines; Chromophores; Fluorophores.

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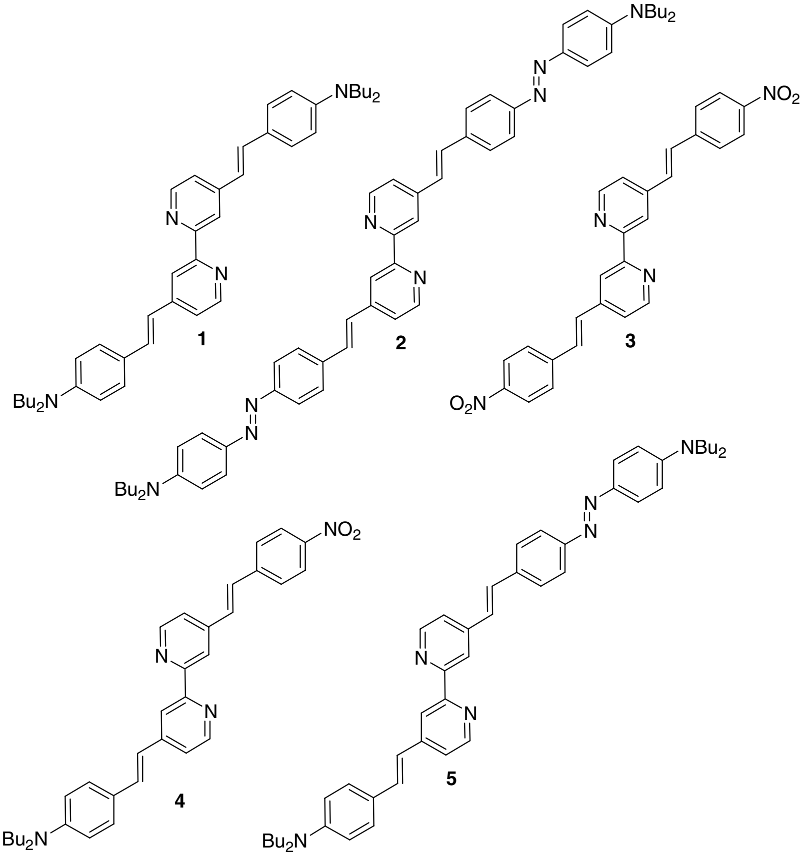
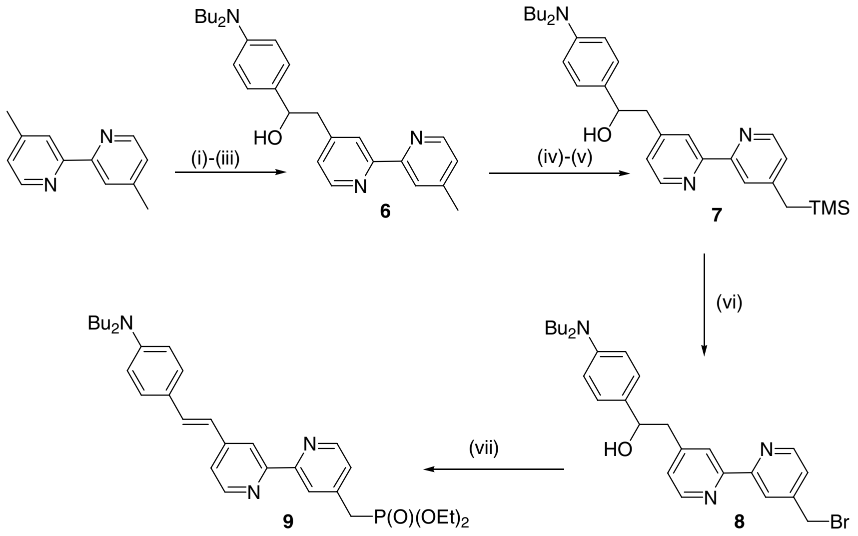
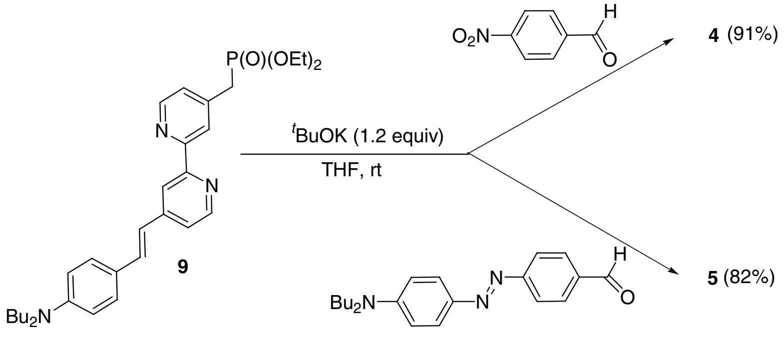


Scheme 1. Structures of bichromophoric bipyridines **4**, **5** and of the parent ligands **1**–**3**.



Scheme 2. Reagents and conditions: (i) LDA (1.1 equiv), THF, −78 °C; (ii) *p*-dibutylaminobenzaldehyde, THF, −78 °C, 1 h; (iii) H_2O, rt, 97%; (iv) LDA (2.2 equiv), 20 min, −78 °C; (v) Me_3SiCl (1 equiv), −78 °C, 2 min followed by EtOH (10 ml), 90%; (vi) $C_2Br_2F_4$ (3.8 equiv), DMF, rt, 10 min followed by CsF (4 equiv), 20 min, 92% and (vii) $P(OEt)_3$ (15 equiv), $CHCl_3$, reflux, 3 h; PPTS (0.1 equiv), reflux, 3 h, 80%.

The synthesis of unsymmetrically substituted ligands **4** and **5** is shown in Scheme 3. They were prepared in excellent yield by means of a Wadsworth–Emmons reaction between synthon **9** and the corresponding benzaldehyde derivatives. Their structures were unambiguously confirmed by ^{1}H NMR spectroscopy.[11,12] In particular,



Scheme 3. Synthesis of ligands **4** and **5**.

Table 1. Photophysical data (absorption and emission)[a]

Compound	λ_{abs} (nm)	ε (L mol^{-1} cm^{-1})	λ_{em} (nm)	Stokes shift (nm)
1	401	65,000	497	97
3	480	76,500	—[b]	—
4	400	30,200	495	95
5	408, 470 (sh)	43,000	502	94

[a] Performed at 298 K in diluted dichloromethane solution (ca. 10^{-5}–10^{-6} mol L^{-1}).

[b] Non emissive.

they display two different AB systems for the vinylic protons with typical coupling constants ($^3J_{HH} \approx 16$ Hz) for all-trans (*E*) isomers.

The UV–visible and emission spectra of ligands **4** and **5** have been measured in dichloromethane and the results are presented in Table 1 and Figures 1 and 2. The spectra feature intense π–π* transitions in the UV region together with broad charge transfer bands in the visible region. In the visible, the absorption spectrum of **4** is almost similar to that of **1**, except the molar absorptivity which is half. Similarly, the emission maximum of **4** is observed at the same wavelength as that of **1**, showing that the emission occurs only from the *p*-dibutylaminostyryl pyridine sub-chromophore. These observations indicate that there is no electronic interaction between the donor and acceptor moieties, as expected by their *meta*-arrangements with respect to the 2,2′-bipyridine bridge. Bipyridine **5** exhibits an intense broad band with λ_{max} at 408 nm and a shoulder at ca. 470 nm. A comparison with the optical data of **1** and **3** clearly shows that the absorption spectrum of **5** consists in the overlap of the absorptions of the two different sub-chromophoric units. Like compounds **1** and **4**, **5** exhibits a structureless fluorescence band at ca. 500 nm, and the excitation spectrum ($\lambda_{exc} = 395$ nm) closely matches the absorption spectrum of **1** (Fig. 2).

In conclusion, we have prepared two new bipyridine chromophores by using a stepwise functionalization of 4,4′-dimethyl-2,2′-bipyridine, a methodology which could provide access to a family of unsymmetrically substituted bipyridines. The use of these ligands for the construction of new octupolar metal NLO-phores is under investigation.

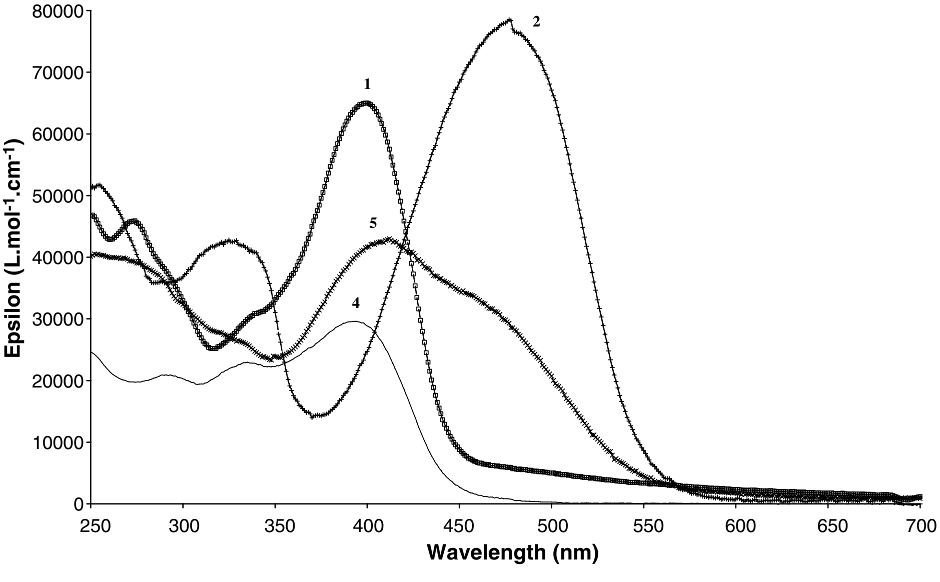


Figure 1. UV–visible absorption spectra of **1**, **2**, **4** and **5** in CH_2Cl_2 at room temperature.

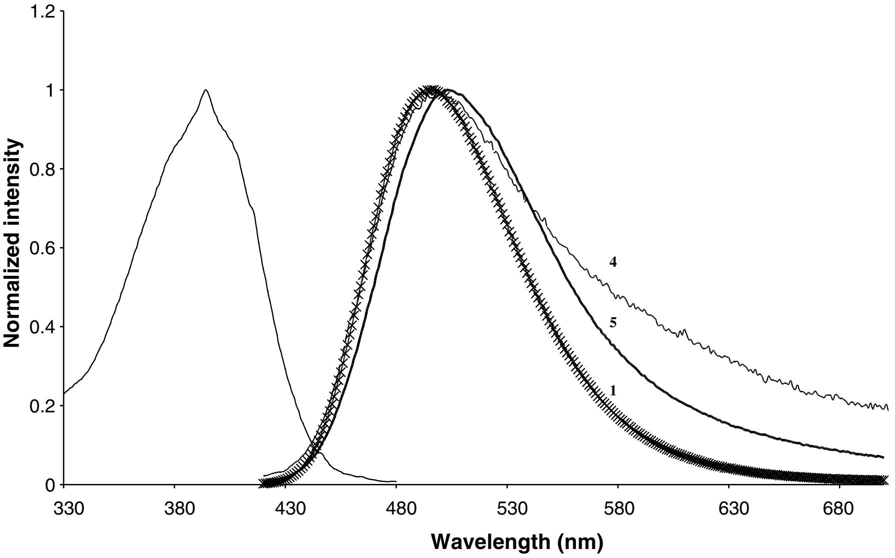


Figure 2. Normalized emission spectra of **1**, **4** and **5** upon excitation at 400 nm in CH_2Cl_2 at room temperature (right); excitation spectrum of **4** (left).

Acknowledgements

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10. *Selected data for* **9**: ^{1}H NMR (500.13 MHz; $CDCl_3$) δ (ppm): 8.64 (d, $J = 5.0$ Hz, 1H); 8.62 (d, $J = 5.0$ Hz, 1H); 8.45 (s, 1H); 8.32 (s, 1H); 7.50–7.25 (m, 4H); 7.19 (d, $J = 16.6$ Hz, 1H); 6.86 (d, $J = 16.6$ Hz, 1H); 6.61 (d, $J = 8.8$ Hz, 2H); 4.08 (qt, $J = 7.9$ Hz, 4H); 3.27 (t, $J = 7.2$ Hz, 4H); 3.23 (d, $J_{P-H} = 22.4$ Hz, 2H); 1.61–1.46 (m, 4H); 1.43–1.22 (m, 4H); 1.07 (t, $J = 7.2$ Hz, 12H); ^{31}P NMR (81.02 MHz; $CDCl_3$) δ (ppm): 25.75; HRMS (EI) $[M-H_2O]^+$ calcd for $C_{31}H_{42}N_3O_3P$. Found 535.2963 (535.2944).
11. *Selected data for* **4**. ^{1}H NMR (500.13 MHz, CD_2Cl_2) δ (ppm): 8.73 (d, $J = 5.0$ Hz, 1H); 8.60 (d, $J = 5.0$ Hz, 1H); 8.59 (s, 1H); 8.49 (s, 1H); 8.27 (d, $J = 8.7$ Hz, 2H); 7.70 (d, $J = 8.7$ Hz, 2H); 7.50 (d, $J = 16.6$ Hz, 1H); 7.46 (d, $J = 8.7$ Hz, 2H); 7.42 (d, $J = 16.6$ Hz, 1H); 7.40–7.38 (m, 2H); 7.30 (d, $J = 16.6$ Hz, 1H); 6.92 (d, $J = 16.6$ Hz, 1H); 6.67 (d, $J = 8.7$ Hz, 1H); 3.34 (t, $J = 7.7$ Hz, 4H); 1.62 (qt, $J = 7.7$ Hz, 4H); 1.40 (st, $J = 7.5$ Hz, 4H); 1.00 (t, $J = 7.5$ Hz, 6H); HRMS (ESI) $[M+H]^+$ calcd for $C_{34}H_{37}N_4O_2$. Found 533.9165 (533.9130).
12. *Selected data for* **5**. ^{1}H NMR (500.13 MHz, CD_2Cl_2) δ ppm: ^{1}H NMR (500.13 MHz, CD_2Cl_2) δ ppm: 8.70 (d, $J = 5.0$ Hz, 2H) 8.60 (s, 2H); 7.96 (d, $J = 16.2$ Hz, 1H); 7.91–7.68 (m, 3H); 7.57 (d, $J = 16.4$ Hz, 1H); 7.53–7.34 (m, 5H); 7.29 (d, $J = 16.2$ Hz, 1H); 6.95 (d, $J = 16.4$ Hz, 1H); 6.75 (d, $J = 9.2$ Hz, 2H); 6.72 (d, $J = 8.7$ Hz, 4H); 3.36 (t, $J = 7.2$ Hz, 8H); 1.77–1.53 (m, 8H); 1.52–1.27 (st, $J = 7.2$ Hz, 8H); 1.01 (t, $J = 7.2$ Hz, 12H); HRMS (ESI) $[M+H]^+$ calcd for $C_{34}H_{37}N_4O_2$. Found 719.4801 (719.4802).