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. Another interest is their uses as building blocks for the construction of efficient molecular and macromolecular nonlinear optical (NLO) chromophores. 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. 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) and very recently the photoisomerizable p-dibutylaminophenylazostyril group (2). 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). 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 D3 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. Finally the phosphonate derivative 9 was synthesized in good yield (80%) by means of an Arbuzov reaction.
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,
they display two different AB systems for the vinylic protons with typical coupling constants ($3J_{HH}$) = 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 $\pi-\pi^*$ 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 the emission occurs only from the $p$-dibutylamino-styryl 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 $\lambda_{\text{max}}$ 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 ($\lambda_{\text{exc}} = 395$ 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.

![Scheme 3. Synthesis of ligands 4 and 5.](image)

**Table 1. Photophysical data (absorption and emission)**

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{\text{abs}}$ (nm)</th>
<th>$\varepsilon$ (L mol$^{-1}$ cm$^{-1}$)</th>
<th>$\lambda_{\text{em}}$ (nm)</th>
<th>Stokes shift (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>401</td>
<td>65,000</td>
<td>497</td>
<td>97</td>
</tr>
<tr>
<td>3</td>
<td>480</td>
<td>76,500</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>4</td>
<td>400</td>
<td>30,200</td>
<td>495</td>
<td>95</td>
</tr>
<tr>
<td>5</td>
<td>408, 470 (sh)</td>
<td>43,000</td>
<td>502</td>
<td>94</td>
</tr>
</tbody>
</table>

*Performed at 298 K in diluted dichloromethane solution (ca. $10^{-3}$ - $10^{-6}$ mol L$^{-1}$).

$b$ Non emissive.

![Figure 1. UV-visible absorption spectra of 1, 2, 4 and 5 in CH$_2$Cl$_2$ at room temperature.](image)
Acknowledgements

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References and notes

10. Selected data for 9. 1H 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, Jp/C0H = 22.4 Hz, 2H); 1.61–1.46 (m, 4H); 1.43–1.22 (m, 4H); 1.07 (t, J = 7.2 Hz, 12H); 31P NMR (81.02 MHz; CDCl 3) δ (ppm): 25.75; HRMS (EI) [M+H]+ calcd for C31H42N3O3P. Found 535.2963 (535.2944).
11. Selected data for 4. 1H NMR (500.13 MHz, CD2Cl2) 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, 8H); 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 C34H37N4O2. Found 533.9165 (533.9130).
12. Selected data for 5. 1H NMR (500.13 MHz, CD2Cl2) 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 C34H37N4O2. Found 719.4801 (719.4802).

Figure 2. Normalized emission spectra of 1, 4 and 5 upon excitation at 400 nm in CH2Cl2 at room temperature (right); excitation spectrum of 4 (left).