A new class of bipyrimidine-based octupolar chromophores: synthesis, fluorescent and quadratic nonlinear optical properties†

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New D_{2d} octupolar organic chromophores based on bipyrimidine as a strong acceptor group exhibit strong fluorescence, fluorosolvatochromism and large second-order nonlinear optical responses.

Interest in nonlinear optics (NLO) has led to the design of chromophores with large molecular hyperpolarizability, mainly one-dimensional (1D) dipolar chromophores.[1] More recently, nondipolar molecules have attracted much attention since the discovery in the early 1990s of the enlarged potential of 2D and 3D octupolar chromophores, especially in terms of easier noncentrosymmetric arrangements and an improved transparency/optical nonlinearity trade-off with respect to traditional dipolar chromophores.[2] Thus, the quadratic optical nonlinearities of a large number of 2D organic and organometallic compounds of D_3 and D_{3h} symmetry have been reported so far.[3–7] In contrast, a relatively small number of 3D tetrahedral (T_d) or pseudo-tetrahedral (D_{2d}) molecules have been investigated as NLO-phores.[8]

During the last decade, our group has been working on the quadratic NLO properties of octupolar, either octahedral (D_3) or pseudo-tetrahedral (D_{2d}), metal complexes featuring 4,4′-π-donor-substituted 2,2′-bipyridine ligands (Fig. 1).[9]

In addition, we have demonstrated that, owing to their synthetic flexibility, such types of ligand allow the fine-tuning of their optical properties through simple changes to the π-conjugated backbone.[10]

Continuing our work towards chromophores based on functionalized heteroaryl molecules, we now turn our attention to bipyrimidine derivatives, which seem very attractive for the following reasons: (i) the electron affinity of the pyrimidine ring is much higher than that of the pyridine ring, and this property has recently been exploited for the design and synthesis of pyrimidine-containing π-conjugated systems with interesting luminescent and two-photon absorption properties;[11] (ii) because of electronic repulsion between the lone pairs on the nitrogens, the two pyrimidine units should not be in the same plane, thus allowing the molecule to present a pseudo-tetrahedral octupolar symmetry; (iii) they can be used as versatile bis-chelate ligands towards metal ions and important building blocks for the construction of supramolecular assemblies.[12,13] In this Letter, we wish to disclose our preliminary results on the synthesis, fluorescent and quadratic NLO properties of new donor-substituted styryl bipyrimidine derivatives.

Scheme 1 depicts the synthetic pathways we used to prepare compounds **4** and **5**. 4,4′,6,6′-Tetramethyl-[2,2′]-bipyrimidine (**3**) was synthesized according to previously reported procedures by the nickel-catalyzed self-coupling reaction of 2-chloro-4,6-dimethyl-pyrimidine.[14] The target bipyrimidines **4** (R = NEt_2) and **5** (R = NPh_2) were readily prepared by means of a quadruple Knoevenagel condensation between **3** and the corresponding aminobenzaldehyde derivatives in the presence of tBuOK (Scheme 1).

This coupling reaction afforded derivatives **4** and **5** as orange-red microcrystals (yield ~ 70%), which were fully characterized by ^{1}H NMR, ^{13}C NMR, UV-vis and emission spectroscopies, and by X-ray crystallography.

Orange crystals suitable for X-ray diffraction analysis were obtained by the slow diffusion of pentane into a dichloromethane solution of **4** (see the ESI for selected bond lengths and angles, crystal data and refinement parameters†). The ligand crystallizes with one molecule of dichloromethane, and the structure consists in interpenetrated and alternating molecules, **4A** and **4B**, differing by the twist angles between their pyrimidine rings (Fig. 2). Both independent bipyrimidine systems have a crystallographically-imposed two-fold symmetry ($P2/n$). As expected, the two molecules adopt a distorted tetrahedral geometry, but with a different torsion angle N_1–C_1–C_{1i}–N_{2i} of 73.72° for **4A** (Fig. 3) and 36.08° for **4B**, probably because of crystal packing forces.

The *E*-configuration of the double bonds, and the *s-trans* conformation between the double bonds and the bipyrimidine

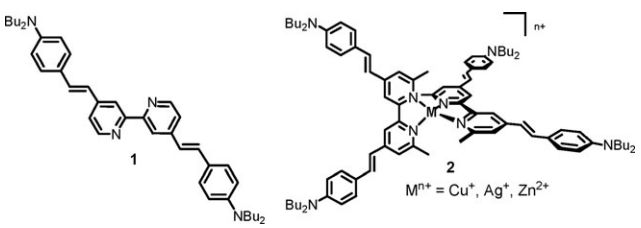

Fig. 1 The chemical structures of representative bipyridyl pro-ligand **1** and pseudo-tetrahedral metal complexes **2**.

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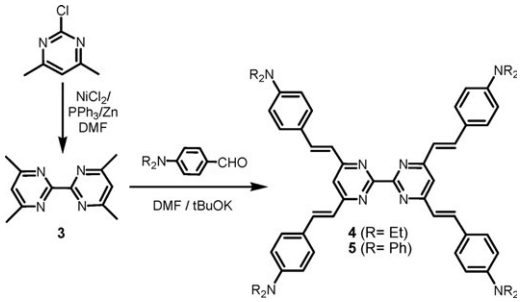
† Electronic supplementary information (ESI) available: Experimental procedures and characterisations, details of the crystallographic structure of **4** (CCDC 707590). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b907323j



Scheme 1 The synthesis of bipyrimidine derivatives **4** and **5**.

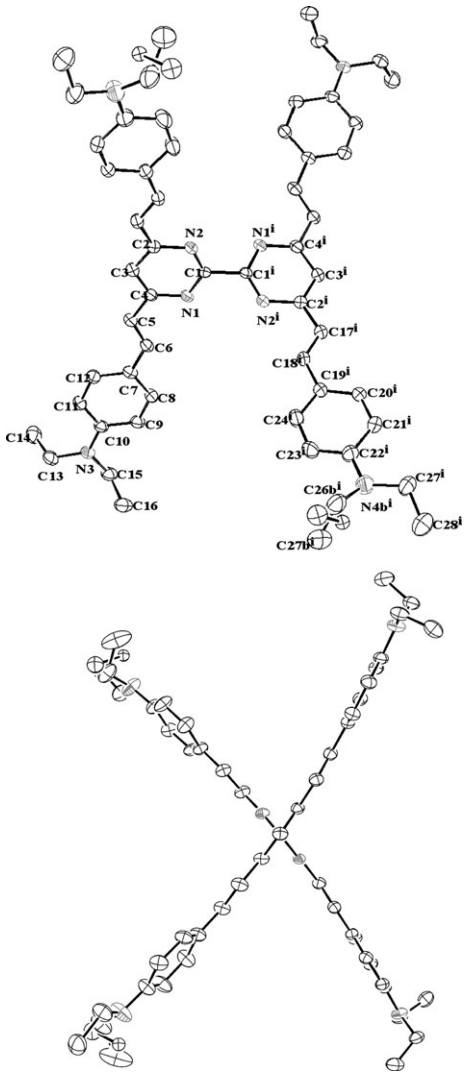


Fig. 2 An ORTEP drawing of compound **4** (molecule **4A**) (50% probability thermal ellipsoids); for clarity, solvent molecules are omitted. The additional "i" letters in the atom labels indicate that these atoms are at equivalent positions ($\frac{3}{2} - x$, y, $\frac{1}{2} - z$).

ring bonds are confirmed. The planarity in the solid state can be estimated by measuring the torsion angle, τ, between the phenyl and pyridyl rings. Assuming that the C4–C5–C6–C7 atoms are coplanar, τ is the algebraic sum of torsion angles C3–C4–C5–C6 and C5–C6–C7–C12. In the structure, τ is found to be 6.3° for C4–C5–C6–C7 and 9.3° for

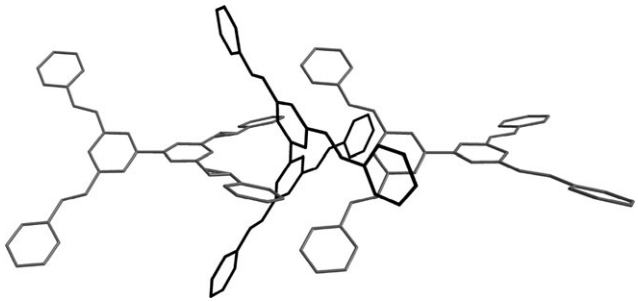


Fig. 3 An ORTEP drawing of compound **4** (gray: molecule **4B**; black: molecule **4A**); for clarity, solvent molecules and NEt_2 groups are omitted.

C2i–C17i–C18i–C19i, clearly indicating the good planarity of the π-conjugated systems. Moreover, the C4–C5 and C5–C6 bond lengths fall between those of classical single and double bonds, indicating good delocalization along the π-conjugated backbone.

The photophysical properties of the bipyrimidine derivatives are given in Table 1, whilst the absorption and emission spectra of **4** are presented in Fig. 4. The UV-vis absorption spectra of **4** and **5** in dichloromethane display an intense broad band at λ = 437 and 421 nm, respectively, which can be ascribed to an intramolecular charge-transfer (ICT) transition. Replacement of the diethylamino donor by the weaker diphenylamino donor leads to a blue shift of the absorption maxima by 16 nm. A comparison of the λ_{max} of **4** with that of related 4,4′-bis(dibutylaminostyryl)-2,2′-bipyridine (**1**) (λ_{max} = 401 nm in dichloromethane)[10b] reveals a significant red shift of the ICT band ($\Delta\lambda$ = 36 nm), as expected from the stronger electron acceptor character of the pyrimidine *vs.* the pyridine core. Compounds **4** and **5** are also strongly fluorescent in dichloromethane at 298 K, with the fluorescence quantum yield ranging from 0.29 to 0.52. Note that the λ_{em} of **5** (donor = NPh_2) shows a greater bathochromic, and hence a larger Stokes, shift (Table 1) in comparison to **4** (donor = NEt_2), indicating a substantial planarization of the excited state and a more pronounced charge-transfer for **5** than for **4**.

Solvatochromic and fluorosolvatochromic measurements were performed using six different solvents (see the ESI†). Interestingly, they exhibited strong positive fluorosolvatochromism; increasing the polarity of the solvent lead to a pronounced red shift of the emission band (for **4**: λ_{em}(cyclohexane) = 477 nm; λ_{em} (CH_3CN) = 591 nm), consistent with a charge-transfer character for the fluorescent singlet excited state (Fig. 5).

The harmonic light scattering (HLS) technique was used for molecular first hyperpolarizability (β) measurements. The measurements were performed in chloroform at a fundamental wavelength of 1.64 μm, provided by an optical parametric oscillator (OPO) pumped at 355 nm by a frequency-tripled nanosecond Nd:YAG laser. Using this wavelength ensured that any contribution to the HLS signal from two-photon fluorescence became negligible, as its harmonic at 820 nm lies far from the fluorescence domain. The values of $\beta_{1.64}$ and static hyperpolarizability β_0 for **4** and **5** are given in Table 1. These data clearly show the good quadratic NLO activity of

Table 1 Optical and NLO data of bipyrimidines **4** and **5** and compounds **1** and **2**

Compound	λ_{abs}/nm[a] (ε_{max})[b]	λ_{em}/nm	Φ_{em}[c]	Stokes shift/cm^{-1}	$\beta_{1.64}/10^{-30}$ esu[d]	$\beta_0/10^{-30}$ esu[e]
4	437 (130)	554	0.52	4833	166	110
5	421 (77)	560	0.29	5893	190	130
1[f]	401 (65)	497	0.22	4816	—	—
2 (M = Ag)[g]	431 (115)	562	—	5509	90[h]	70

[a] In dichloromethane. [b] Units: 10^3 mol^{-1} cm^{-1}. [c] Fluorescence quantum yield with ±10% error. [d] Measured by HLS (precision ±10%) in $CHCl_3$ solution (units: 10^{-3} mol L^{-1}). [e] Deduced from a three-level model. [f] Ref. 10*b*. [g] Ref. 9*d*. [h] Measured by HLS at 1.91 mm in dichloromethane.

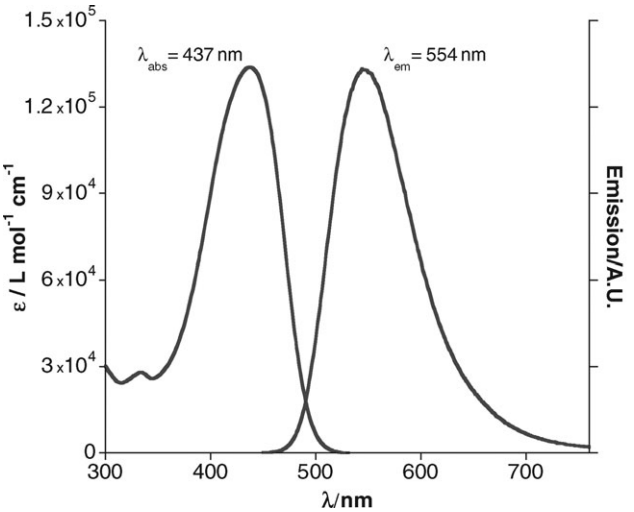


Fig. 4 Absorption and normalised emission spectra of **4** in dichloromethane.

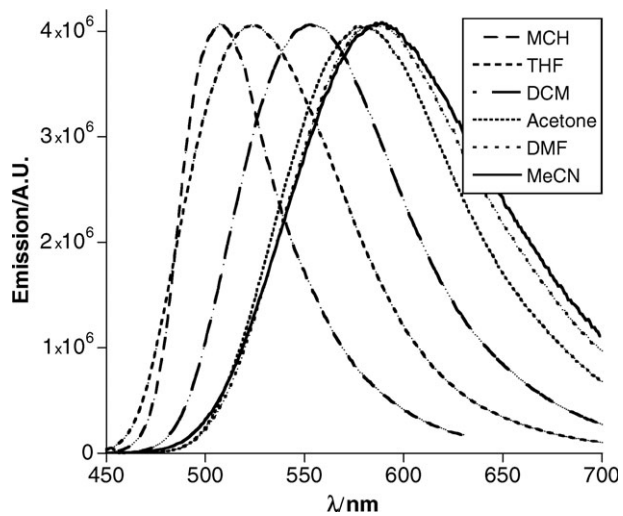


Fig. 5 Fluorosolvatochromic measurements of **4** performed using six different solvents.

these new multipolar chromophores. We also note that replacing the diethylamino donor group by the weaker diphenylamino donor group results in *ca.* 20% enhancement in the β_0 value. This effect of alkyl *vs.* aryl substitution on the molecular hyperpolarizability has already been observed in push–pull derivatives and explained by enhanced π-conjugation in the case of diarylamino donor groups.[15] Finally, comparison of the hyperpolarizability values of **4** and **5** with those of pseudo-tetrahedral bis(bipyridine) metal complexes **2**[9d] (Table 1) clearly shows the efficiency of these bipyrimidine derivatives in terms of an improved transparency/nonlinearity trade-off, since, for example, **5** exhibits a β_0 value that is roughly two times larger than that of complex **2** when M = Ag.

In summary, we have prepared new D_{2d} octupolar chromophores based on bipyrimidine as a strong acceptor group. Such derivatives exhibit interesting fluorescence and fluorosolvatochromic properties, as well as large second-order NLO responses. Finally, these derivatives open up new opportunities for the construction of supramolecular assemblies upon coordination to metal ions. Studies in this field, particularly with regard to new NLO materials with intrinsic octupolar organization, are in progress.

Experimental

Preparation of 4

4,4′,6,6′-Tetramethyl-[2,2′]-bipyrimidine (**3**) (100 mg, 0.46 mmol) and 4-diethylaminobenzaldehyde (489 mg, 2.76 mmol; 6 equiv.) were dissolved in tetrahydrofuran (10 mL) in a Schlenk flask. tBuOK (300 mg, 2.67 mmol) was slowly added at room temperature. The solution, which immediately turned brown, was then refluxed overnight. The addition of water led to the formation of a pale brown mixture. The tetrahydrofuran was evaporated, and the mixture extracted with dichloromethane, dried over $MgSO_4$ and the solvent removed under vacuum. Recrystallization from a dichloromethane–pentane mixture gave **4** as an orange microcrystalline powder (300 mg, 76%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.90 (d, J = 16.1 Hz, 4H), 7.60 (d, J = 8.1 Hz, 8H), 7.48 (s, 2H), 7.11 (d, J = 15.8 Hz, 4H), 6.71 (d, J = 7.9 Hz, 8H), 3.43 (q, J = 7.2 Hz, 16H) and 1.23 (t, J = 7.2 Hz, 24H). ^{13}C NMR ($CDCl_3$): δ 12.43, 44.43, 111.42, 113.35, 120.94, 122.96, 129.40, 136.99, 148.73, 163.82 and 164.21. TGA: Td_5 = 390 °C. Anal. found: C, 77.81; H, 7.79; N, 12.88; $C_{56}H_{66}N_8{\cdot}\frac{1}{4}CH_2Cl_2$ requires C, 77.44; H, 7.77; N, 12.84%. MS (Zabspec-TOF) m/z = 851.5496 $[M + H]^+$; $C_{56}H_{67}N_8$ requires 851.5488.

X-ray diffraction study of 4

Single crystals suitable for X-ray crystal analysis were obtained by the slow diffusion of pentane into a dichloromethane solution of **4** at room temperature. Crystals were removed from their mother solution, coated with oil and rapidly transferred to the diffractometer in order to prevent solvent evaporation. $C_{56}H_{66}N_8{\cdot}2CH_2Cl_2$, M = 1021.02, monoclinic $P2/n$, a = 17.5345(15), b = 15.2814(14), c = 20.3953(18) Å, β = 96.350(5)°, V = 5431.4(8) Å^3, Z = 4,

ρ_{calc} = 1.249 g cm^{-3}, μ(Mo-K$_\alpha$) = 0.264 mm^{-1}; the structure, refined on $F2$, converged for 12 438 unique reflections (R_{int} = 0.0481) and 8362 observed reflections with $I > 2\sigma(I)$ to give $R1$ = 0.073, w$R2$ = 0.2204 and goodness-of-fit S = 1.151.†

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