Supplementary Material (ESI) for New Journal of Chemistry

Supporting Information

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

H. Akdas-Kilig[a], T. Roisnel[a], I. Ledoux[b], and H. Le Bozec*[a]

---

[a] Organométalliques et Matériaux Moléculaires, UMR 6226
CNRS-Université de Rennes 1, Campus de Beaulieu, 35042 Rennes cedex (France)
Fax: (+) 00 33 (0)2 23 23 69 39 E-mail: hubert.le-bozec@univ-rennes1.fr
[b] Laboratoire de Photonique Quantique et Moléculaire (UMR CNRS 8537)
ENS Cachan,61 avenue du Président Wilson, 94235 Cachan (France)

Experimental procedures

NMR spectra (^{1}H, ^{13}C) were recorded at room temperature on BRUKER DPX200 and DMX500 spectrometers operating at 200.12 and 500.13 MHz. UV-Visible spectra were recorded on a Cary 5000 spectrophotometer. High-resolution mass spectra were obtained on a Varian MAT 311 or ZabSpec TOF Micromass instrument at CRMPO, University of Rennes 1. Elemental analyses were performed by the CRMPO, University of Rennes 1. Luminescence Measurements: The emission spectra were recorded on a Photon Technology International (PTI) SE-900m spectrofluorimeter. Fluorescence experiments were performed in dilute dichloromethane solution (ca. 10^{-6}-10^{-7} mol L^{-1}). Fluorescence quantum yields were measured on non-degassed samples at room temperature. Solutions of Fluorescein in NaOH (1 M) were used as standard for the quantum yield measurement (Φ_F.0.90). Refractive index corrections have been performed. HLS measurements were performed in $CHCl_3$ at 1.64 µm, using a nanosecond laser source made of an OPO pumped by a frequency-tripled Nd:YAG source, operating at a 10 Hz repetition rate. Solutions of the molecules to me measured are placed in a fluorimetric cell and illuminated by a focused IR beam at 1.64 µm with variable incident intensity. The corresponding harmonic Light scattering at 820 nm is collected at 90° with respect to the incident beam, then filtered and detected by an IR-sensitive photomultiplier from Hamamatsu, and processed by a Boxcar coupled to a computer. This second harmonic signal is recorded as a function of a "reference" harmonic beam obtained by frequency doubling a part of the same laser souce by the strongly nonlinear organic powder. From the slope of the resulting line we infer the HLS hyperpolarizability of the dissolved molecules, by comparing their HLS emission with that of a solution of a standard NLO molecule, Ethyl violet ($\beta = 230.10^{-30}$ esu at 1.64 µm). The error in the measurements is estimated to be ±10%.

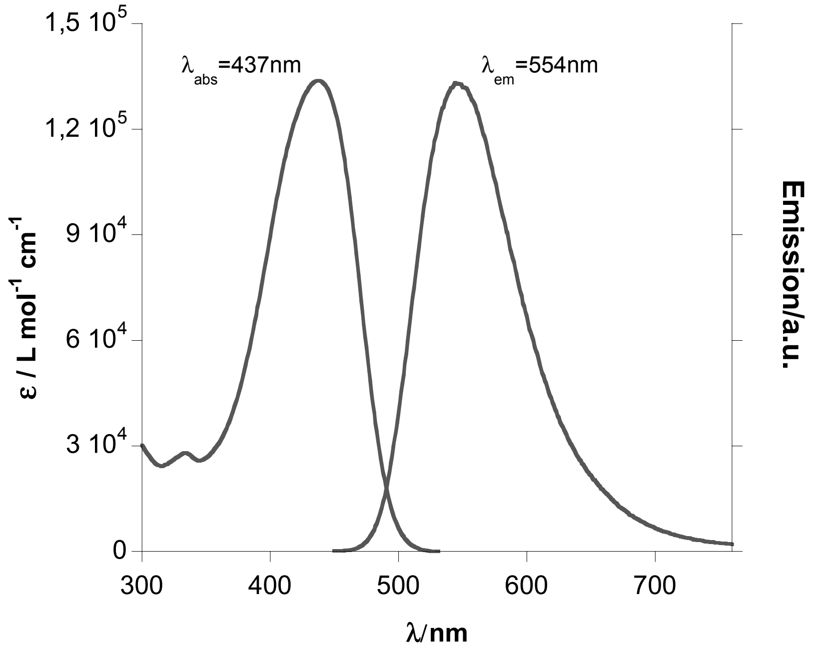
4,4',6,6'-Tetrakis(N,N-diphenylaminostyryl)-[2,2']-bipyrimidine (5). Compound **5** was prepared according to the above procedure, from 3 (50 mg, 0.23 mmol), 4-diphenylaminobenzaldehyde (382 mg, 1.4 mmol, 6 equiv.) and tBuOK (158 mg,13.55 mmol) in tetrahydrofuran (10 mL). Work-up as above gave **5** as a orange-red microcrystalline powder (200 mg, 70%).^{1}H NMR ($CDCl_3$, 500 MHz): 7.98 (d, $J = 16$ Hz, 4H), 7.58 (d, $J = 8$ Hz, 8H), 7.48 (s, 2H), 6.7-7.2 (m, 48H). TGA: Td_5 = 435°C. Anal. found: C, 80.71; H, 5.13; N, 8.53. $C_{88}H_{66}N_8{\cdot}CH_2Cl_2$. Calc.: C, 80.95; H, 5.19; N, 8.49. *m/z* (Zabspec-TOF) 1235.5475 ; ($[M+H]^+$, $C_{88}H_{67}N_8$ requires 1235.5488).

Supporting Table 1. Solvatofluorochromic behavior of **4** and **5**

Solvent	**4** λ_{max}/nm	**4** λ_{em}/nm[a]	**5** λ_{max}/nm	**5** λ_{em}/nm[a]
C_7H_{15}	412	477	414	497
THF	425	524	412	537
CH2Cl2	437	554	421	569
Acetone	433	565	413	575
DMF	441	581	414	594
MeCN	436	591	424	604

[a] Fluorescence experiments were performed in dilute dichloromethane solution (ca. 10^{-6}-10^{-7} mol L^{-1}) using a PTI spectrometer.

Supporting Figure 1. Absorption and normalised emission spectra of **5** in dichloromethane



Crystal structure analysis

Single crystals suitable for X-Ray crystal analysis were obtained by 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.

(C56 H66 N8, 2 C H2 Cl2); M = 1021.02. APEXII, Bruker-AXS diffractometer, Mo-Kα radiation (λ = 0.71073 Å), T = 100(2) K; monoclinic P 2/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, d = 1.249 $g.cm^{-3}$, μ = 0.264 mm^{-1}. The structure was solved by direct methods using the SIR97 program [1], and then refined with full-matrix least-square methods based on F^2 (SHELX-97) [2] with the aid of the WINGX [3] program. The contribution of the disordered solvents to the calculated structure factors was estimated following the BYPASS algorithm [4], implemented as the SQUEEZE option in PLATON {5]. A new data set, free of solvent contribution, was then used in the final refinement. All non-hydrogen atoms were refined with anisotropic thermal parameters. H atoms were finally included in their calculated positions. A final refinement on F^2 with 12438 unique intensities and 624 parameters converged at $\omega R(F^2) = 0.2204$ (R(F) = 0.073) for 8362 observed reflections with $I > 2\sigma(I)$.

[1] A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Cryst.* 1999, **32**, 115-119.
[2] SHELX97 - Programs for Crystal Structure Analysis (Release 97-2). G. M. Sheldrick, Institüt für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany,1998.
[3] L. J. Farrugia, *J. Appl. Cryst.*, 1999, **32**, 837-838
[4] Sluis, P. v.d. & Spek, A. L. (1990) *Acta Cryst.* **A46**, 194-201
[5] A. L. Spek, *Acta Cryst.*, 1990, **A46**, C34.

Table 1. Selected crystallographic and data collection parameters for **4**[a]

Empirical formula	C56 H66 N8, 2 C H2 Cl2
Formula weight	1021.02
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, P 2/n
Unit cell dimensions	a = 17.5345(15) Å, alpha = 90 °
	b = 15.2814(14) Å, beta = 96.350(5) °
	c = 20.3953(18) Å, gamma = 90 °
Volume	5431.4(8) Å^{3}
Z, Calculated density	4 , 1.249 (g.cm^{-3})
Absorption coefficient	0.264 mm^{-1}
F(000)	2168
Crystal size	0.55 x 0.5 x 0.37 mm
Theta range for data collection	2.91 to 27.48 °
h_min, h_max	-22, 22
k_min, k_max	-19, 19
l_min, l_max	-26, 26
Reflections collected / unique	103661 / 12438 [R(int) = 0.0481]
Completeness to theta_max	0.998
Absorption correction type	multi-scan
Max. and min. transmission	0.907, 0.892
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12438 / 0 / 626
Goodness-of-fit	1.151
Final R indices [I>2sigma(I)]	R1 = 0.073, wR2 = 0.2204
R indices (all data)	R1 = 0.1004, wR2 = 0.242
Largest diff. peak and hole	0.857 and -0.68 e.A^{-3}

[a] CCDC reference number 707590.

Selected Bond lengths [Å]

N1—C1	1.335(3)	C1—C1i	1.502(4)
N1—C4	1.354(3)	C11—C12	1.383(3)
N2—C1	1.325(3)	C11—C10	1.410(3)
N2—C2	1.366(3)	C10—C9	1.415(3)
C3—C4	1.401(3)	C12—C7	1.413(3)
C3—C2	1.401(3)	C9—C8	1.386(3)
N3—C10	1.379(3)	C8—C7	1.399(3)
N3—C13	1.463(3)	C6—C7	1.454(3)
N3—C15	1.464(3)	C13—C14	1.520(4)
C5—C6	1.348(3)	C15—C16	1.527(4)
C5—C4	1.462(3)		

Selected Angles [°]

C1—N1—C4	115.49(18)
C1—N2—C2	116.38(17)
C4—C3—C2	119.19(19)
C10—N3—C13	120.9(2)
C10—N3—C15	122.43(19)
C13—N3—C15	116.62(18)
N2—C1—N1	128.81(18)
N2—C1—C1i	115.66(18)
N1—C1—C1i	115.52(19)
N3—C10—C11	122.1(2)
N3—C10—C9	121.0(2)
N2—C2—C3	119.4(2)
N1—C4—C3	120.63(18)
N1—C4—C5	117.50(19)
C3—C4—C5	121.84(19)
C5—C6—C7	128.2(2)