

The Effectiveness of Essential-State Models in the Description of Optical Properties of Branched Push-Pull Chromophores

Cristina Sissa,¹ Venkatakrishnan Parthasarathy,^{2,3} Delphine Drouin-Kucma,^{2,3}

Martinus H. V. Werts,^{2,3} Mireille Blanchard-Desce^{2,3} and Francesca Terenziani^{1*}

¹ Dipartimento di Chimica GIAF and INSTM UdR-Parma, Università di Parma, 43124 Parma, Italy

² Université de Rennes 1, CPM (UMR6510), Campus de Beaulieu, Bâtiment 10A, F-35042 Rennes, France

³ CNRS, Chimie et Photonique Moléculaire (UMR6510), 35042 Rennes, France

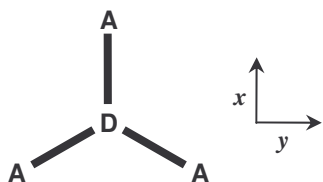
* francesca.terenziani@unipr.it

Supplementary Information

Transition energy and dipole moment in the two-state model for dipolar chromophores:

$$\hbar\omega_{ge} = \sqrt{2}t\sqrt{\frac{1}{\rho(1-\rho)}}; \quad \mu_{ge} = \mu_0\sqrt{\rho(1-\rho)} \quad (\text{S1})$$

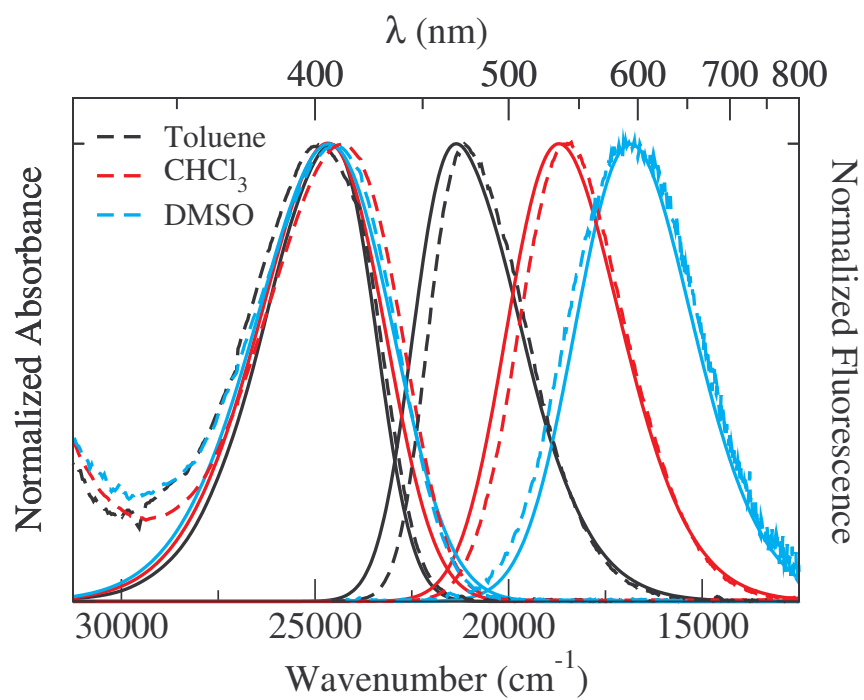
Transition energies and dipole moments in the four-state model for octupolar chromophores:



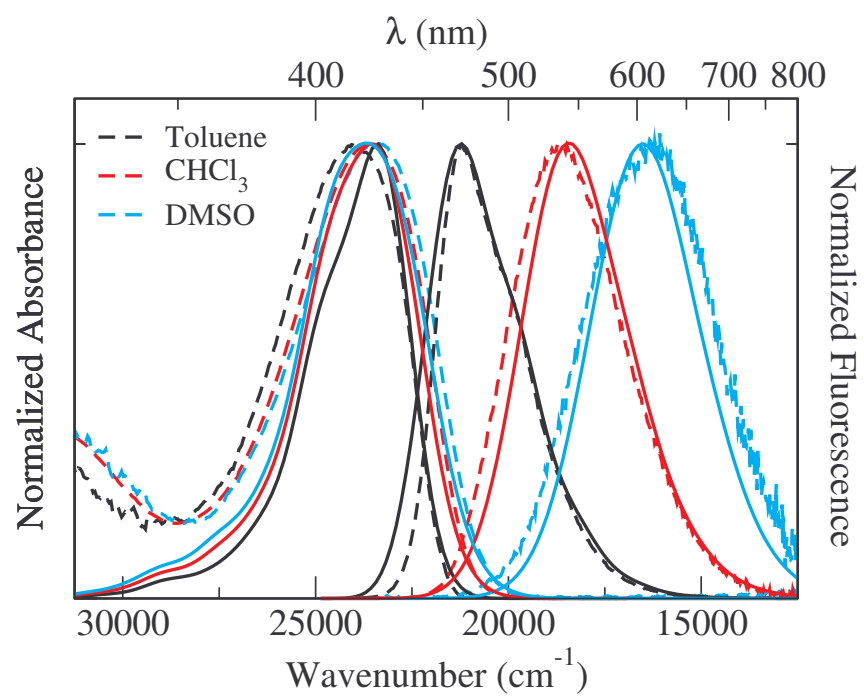
$$\begin{aligned} \hbar\omega_{gc_1} = \hbar\omega_{gc_2} &= \sqrt{6}t\sqrt{\frac{1-\rho}{\rho}}; & \mu_{gc_1}^{(x)} = \mu_{gc_2}^{(y)} &= \mu_0\sqrt{\frac{\rho}{2}}; & \mu_{gc_1}^{(y)} = \mu_{gc_2}^{(x)} &= 0 \\ \hbar\omega_{ge} &= \sqrt{6}t\sqrt{\frac{1}{\rho(1-\rho)}}; & \mu_{ge}^{(x)} = \mu_{ge}^{(y)} &= 0; \\ \hbar\omega_{c_1e} = \hbar\omega_{c_2e} &= \sqrt{6}t\sqrt{\frac{\rho}{1-\rho}}; & \mu_{c_1e}^{(x)} = \mu_{c_2e}^{(y)} &= -\mu_0\sqrt{\frac{1-\rho}{2}}; & \mu_{c_1e}^{(y)} = \mu_{c_2e}^{(x)} &= 0 \\ & & \mu_{c_1c_1}^{(x)} = -\mu_{c_2c_2}^{(x)} = \mu_{c_1c_2}^{(y)} &= \frac{1}{2}\mu_0; & \mu_{c_1c_1}^{(y)} = \mu_{c_2c_2}^{(y)} = \mu_{c_1c_2}^{(x)} &= 0 \end{aligned} \quad (\text{S2})$$

Experimental (dashed lines) and calculated (full lines) absorption and fluorescence spectra

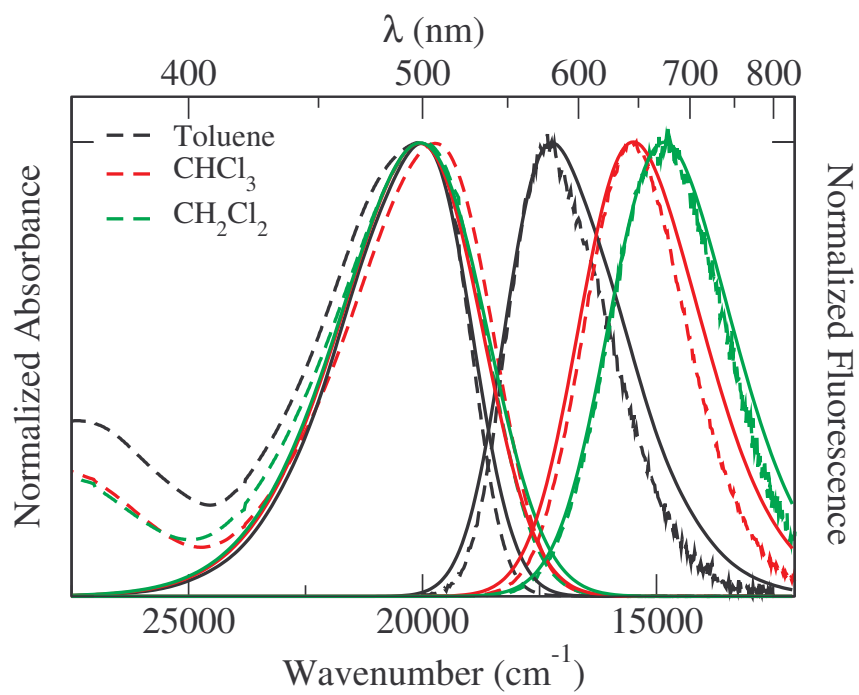
- D1



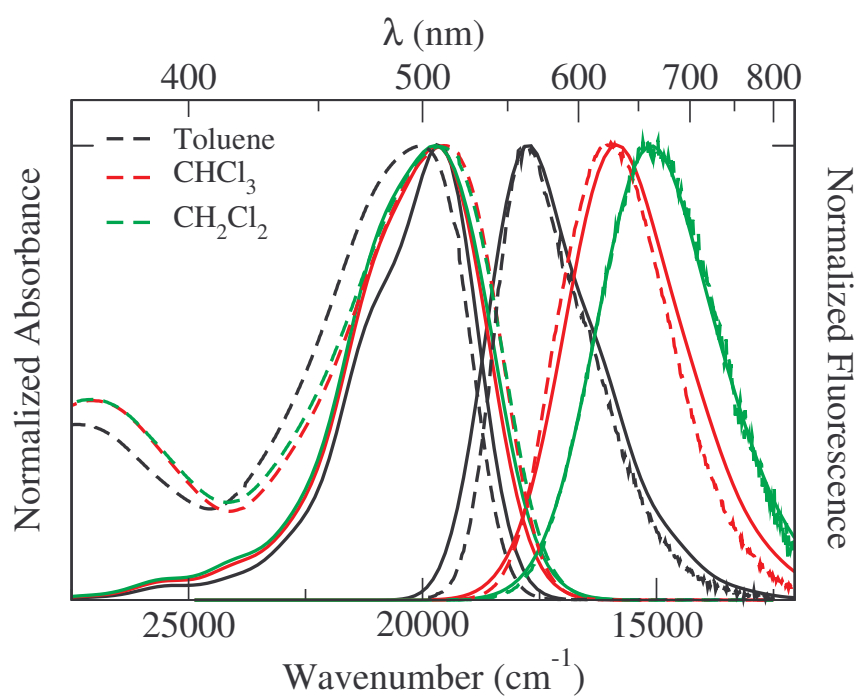
- O1



- D2



- O2



Synthesis

All reactions involving air- or water-sensitive compounds were carried out under argon. Solvents were generally dried and distilled prior to use. Reactions were monitored by TLC on Merck 60 F254 aluminum sheets precoated with silica gel. Column chromatography was performed using Merck silica gel Si 60 (40–63 mm, 230–400 mesh), unless otherwise noted. NMR studies were carried out by Bruker ARX 200 (^1H : 200.17 MHz, ^{13}C : 50.32 MHz) or Avance AV 300 (^1H : 300.13 MHz, ^{13}C : 75.47 MHz), in CDCl_3 solutions; ^1H chemical shifts are given in ppm relative to TMS as internal standard, J values in Hz, and ^{13}C chemical shifts relative to the central peak of CDCl_3 at 77.0 ppm. IR spectra were recorded in Perkin Elmer Spectrum 100 FT-IR spectrometer on solid samples. High-resolution mass spectra were recorded at the Centre Régional de Mesures Physiques de l'Ouest (C.R.M.P.O., Rennes), using a Micromass MS/MS ZABSpec TOF instrument with EBE TOF geometry; liquid secondary ion mass spectrometry (LSIMS) was performed at 8 kV with Cs^+ in *m*-nitrobenzyl alcohol (mNBA). All the compounds were characterized and analyzed by Nuclear Magnetic Resonance spectroscopy (NMR), UV–vis spectroscopy, fluorescence spectroscopy, TPA, HRMS and microanalysis.

The starting materials, such as 4-iodotriphenylamine¹ and 4,4',4''-triiodotriphenylamine,² were prepared according to the literature reported procedures while triphenylamine (Alfa Aesar, 98%) and **O2** (Sigma Aldrich, 97%) used were commercially available.

Synthesis of 4-iodotriphenylamine.¹ To the round bottom flask that was charged with Cu (2.28 g, 36.0 mmol), 18-crown-6 (1.43 g, 5.4 mmol) and K_2CO_3 (9.95 g, 72.0 mmol), was added a solution of diphenylamine (6.09 g, 36.0 mmol) and 1,4-diiodobenzene (41.56 g, 126.0 mmol) in 1,2-dichlorobenzene (26.46 g, 180.0 mmol) under an argon gas atmosphere. The mixture was heated slowly to 180 °C for 64h. After the appropriate reaction time, the reaction mixture was cooled and filtered by silica. The excess 1,2-dichlorobenzene was distilled off and the crude residue was further purified by silica-gel column chromatography using heptane as the eluent to afford 7.8 g (58%) of the required product. ^1H NMR (200.13 MHz, CDCl_3) δ 7.49 (d, J = 8.5 Hz, 2H), 7.26 (m, 4H), 7.07 (m, 6H), 6.82 (d, J = 8.5 Hz, 2H); ^{13}C NMR (50.32 MHz, CDCl_3) δ 147.7, 147.2, 138.0, 129.4, 125.3, 124.5, 123.3, 84.8.

Synthesis of D1.² To an oven dried round bottom flask cooled under argon, was added 4-iodotriphenylamine (0.19 g, 0.5 mmol), 4-formylthiophene-2-boronic acid (0.16 g, 1.0 mmol), anhydrous K_2CO_3 (0.35 g, 2.5 mmol), toluene (1.5 mL) and methanol (1.5 mL), and stirred at room temperature for about 0.25h. Then, $\text{PdCl}_2(\text{dppf})$ (0.04 g, 0.05 mmol) was introduced into the reaction vessel. Now, the whole of the reaction mixture was slowly taken to 75 °C and heated for 6h. The color of the reaction mixture turned brown with time. After the appropriate reaction time, the reaction mixture was cooled and evaporated to dryness. The residue was dissolved in dichloromethane and the organic contents were washed with water and brine. The combined organic extracts were subsequently dried over anhydrous Na_2SO_4 , filtered and evaporated to afford a crude product which was further purified by silica-gel column chromatography using

dichloromethane and heptane mixtures (1:9) to yield 0.164 g (92%) of the desired compound **D1**. The bright yellow solid thus obtained was further recrystallized from dichloromethane and hexane mixtures. IR (cm⁻¹): 1659; ¹H NMR (300.13 MHz, CDCl₃) δ 9.85 (s, 1H), 7.71 (d, *J* = 4.0 Hz, 1H), 7.52 (d, *J* = 9.0 Hz, 2H), 7.26-7.33 (m, 5H), 7.04-7.17 (m, 6H), 7.06 (d, *J* = 9.0 Hz, 2H); ¹³C NMR (75.47 MHz, CDCl₃) δ 182.57, 154.57, 149.14, 146.97, 141.32, 137.71, 129.49, 127.25, 126.14, 125.17, 123.88, 122.86, 122.36; HRMS for M⁺ C₂₃H₁₇NOS: Calcd: 355.10309, Found: 355.1011; Microanalysis for C₂₃H₁₇NOS: Calcd: C, 77.72; H, 4.82; N, 3.94; S, 9.02. Found: C, 77.68; H, 4.77; N, 3.90; S, 9.01.

Synthesis of O1.^{3,4} To an oven dried round bottom flask cooled under argon, was added 4,4',4''-triiodotriphenylamine (0.06 g, 0.09 mmol), 4-formylthiophene-2-boronic acid (0.08 g, 0.5 mmol), anhydrous K₂CO₃ (0.21 g, 1.50 mmol), toluene (1.5 mL) and methanol (1.5 mL), and stirred at room temperature for about 0.25h. Then, PdCl₂(dppf) (0.025 g, 0.03 mmol) was introduced into the reaction vessel. Now, the whole of the reaction mixture was slowly taken to 80-90 °C and heated for overnight. The color of the reaction mixture turned brown with time. After the appropriate reaction time, the reaction mixture was cooled and evaporated to dryness. The residue was dissolved in dichloromethane and the organic contents were washed with water and brine. The combined organic extracts were subsequently dried over anhydrous Na₂SO₄, filtered and evaporated to afford a crude product which was further purified by silica-gel column chromatography using dichloromethane and heptane mixtures to yield 0.05 g (88%) of the desired compound **D1**. The bright yellow compound thus obtained was further recrystallized from dichloromethane and hexane mixtures. IR (cm⁻¹): 1649; ¹H NMR (300.13 MHz, CDCl₃) δ 9.88 (s, 3H), 7.74 (d, *J* = 4.0 Hz, 3H), 7.61 (d, *J* = 8.4 Hz, 6H), 7.36 (d, *J* = 4.0 Hz, 3H), 7.19 (d, *J* = 8.4 Hz, 6H); ¹³C NMR (75.47 MHz, CDCl₃) δ 182.64, 153.62, 147.53, 142.01, 137.57, 128.41, 127.64, 124.63, 123.56; HRMS for [M+H⁺] C₃₃H₂₂NO₃S₃: Calcd: 576.07618, Found: 576.0762.

Synthesis of D2.⁵ A suspension of triphenylamine monoaldehyde **1** (0.03 g, 0.08 mmol) and malononitrile (6.1 × 10⁻³ g, 0.09 mmol) in ethanol (3.0 mL) was subjected to reflux for 40h. The color of the reaction mixture turned from yellow to deep red during the course of the reaction. After completion of the reaction as monitored by TLC, the reaction mixture was cooled and evaporated to afford a residue which was then purified by silica-gel column chromatography using dichloromethane and heptane mixtures as the eluent to obtain a red-brown solid **D2** (0.032g, 93%). The product thus obtained was further recrystallized from dichloromethane and hexane mixtures. IR (cm⁻¹): 2220; ¹H NMR (300.13 MHz, CDCl₃) δ 7.66 (s, 1H), 7.59 (d, *J* = 3.9 Hz, 1H), 7.44 (d, *J* = 9.0 Hz, 2H), 7.17-7.27 (m, 5H), 7.01-7.10 (m, 6H), 6.96 (d, *J* = 9.0 Hz, 2H); ¹³C NMR (75.47 MHz, CDCl₃) δ 157.09, 150.25, 149.87, 146.55, 140.40, 133.02, 129.54, 127.52, 125.46, 124.77, 124.30, 123.23, 121.63, 114.54, 113.65, 74.91; HRMS for M⁺ C₂₆H₁₇N₃S: Calcd: 403.11432, Found: 403.1148; Microanalysis for C₂₆H₁₇N₃S: Calcd: C, 77.39; H, 4.25; N, 10.41; S, 7.95. Found: C, 77.56; H, 4.23; N, 10.16; S, 7.81.

Table S-1. Two-photon excited fluorescence action cross section, $\sigma_2\Phi$, of Nile Red in DMSO, measured using fluorescein (0.01M NaOH), Rhodamine B (methanol) and Styryl-9M (chloroform) as references.⁶ Values were reproducible within +/- 5%.

wavelength / nm	$\sigma_2\Phi$ / GM
990	30.1
1000	32.1
1010	35.1
1020	42.0
1030	56.1
1040	69.0
1050	86.1
1060	92.7
1070	94.2
1080	94.8
1090	95.4
1100	94.7
1110	88.2
1120	76.4
1130	62.0
1140	56.3
1150	55.0
1160	51.5
1170	44.6
1180	38.3
1190	27.2
1200	22.0

- 1 C. Wang, L.-O. Pålsson, A. S. Batsanov and M. R. Bryce, *J. Am. Chem. Soc.* 2006, **128**, 3789-3799.
- 2 D. P. Hagberg, T. Marinado, K. M. Karlsson, K. Nonomura, P. Qin, G. Boschloo, T. Brinck, A. Hagfeldt and L. Sun, *J. Org. Chem.* 2007, **72**, 9550-9556.
- 3 S. Roquet, A. Cravino, P. Leriche, O. Alévêque, P. Frère and J. Roncali, *J. Am. Chem. Soc.* 2006, **128**, 3459-3466.
- 4 A. Cravino, S. Roquet, P. Leriche, O. Alévêque, P. Frère and J. Roncali, *Chem. Commun.* 2006, 1416-1418.
- 5 T. Tominaga, D. Kitazawa, A. Takano and S. Murase, *JP Pat.*, JP2001257077, 2001.
- 6 N. S. Makarov, M. Drobizhev and A. Rebane, *Opt. Express* 2008, **16**, 4029-4047.