

Supporting Information

A multichromophoric dendrimer: from synthesis to energy up-conversion in rigid matrix

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Experimental section

General remarks: ¹H NMR and ¹³C NMR spectra were recorded on a Varian Mercury 400 (¹H: 400 MHz, ¹³C:100 MHz), a Varian Gemini 200 (¹H: 200 MHz, ¹³C: 50 MHz), or a Varian Gemini 300 (¹H: 300 MHz, ¹³C:75 MHz), with tetramethylsilane as internal reference. The chemical shifts (δ) and coupling constants (J) are expressed in ppm and hertz, respectively. IR spectra were recorded on a Perkin–Elmer 881 FT-IR spectrophotometer as KBr pellets. Merck silica gel (0.040–0.063 mm), MP EcoCrhom silica gel (32–63, 60 Å) was used for flash chromatography. TLC were performed on Merck silica gel 60 F254 plates. Elemental analysis were recorded on a Perkin Elmer 240 C,H,N Analyzer. Mass spectra were recorded on a Carlo Erba QMD 1000 for EI (70 eV) and on a Thermo LTQ for ESI. Tetrahydrofuran was distilled over Na/Benzophenone, amines were distilled over KOH. All commercially available reagents and solvents were purchased from Sigma Aldrich and used as received, unless otherwise specified.

Photophysical and photochemical experiments

The experiments were performed at 298 K in CH₃CN solution and in a C₂H₅OH/CH₂Cl₂ 1:1 (v/v) rigid matrix at 77K. Deaerated solutions were obtained by three freeze-pump-thaw cycles.

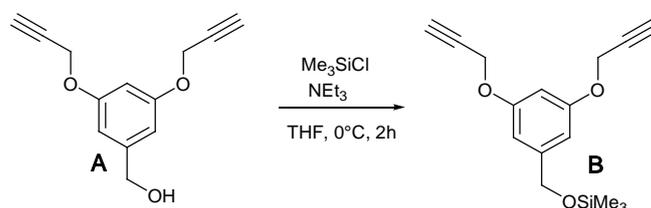
UV-Vis absorption spectra were recorded with a Perkin Elmer λ 40 spectrophotometer, using quartz cells with pathlength 1.0 cm. Emission spectra and phosphorescence lifetimes were obtained with a Perkin Elmer LS-50 spectrofluorimeter, equipped with a Hamamatsu R928 phototube. Emission spectra were corrected for inner filter effects when necessary.¹ Fluorescence quantum yields were measured following the method of Demas and Crosby² (standard used: 9,10-diphenylanthracene, Φ_{em} = 0.90 in deaerated cyclohexane solution and [Ru(bpy)₃]²⁺, Φ_{em} = 0.028 in aerated water solution.).³ Prompt fluorescence lifetimes were measured by time-correlated single-photon counting

(0.5 ns time resolution) with an Edinburgh Instruments DS199 equipment (D_2 lamp). Delayed fluorescence lifetimes were measured by a Hamamatsu R928 phototube connected to a Tektronix TDS380 (400 MHz) oscilloscope upon excitation with a Continuum Surelite I-10 Nd:YAG laser source ($\lambda_{ex} = 532$ nm). The intensity of the laser source was measured by a laser point powermeter model Plus, equipped with a 10 UV-A detector head.

The estimated experimental errors are: ± 2 nm on the band maximum, 5% on the molar absorption coefficient, 10% on the fluorescence quantum yield, 5% on the lifetime.

Synthetic procedures

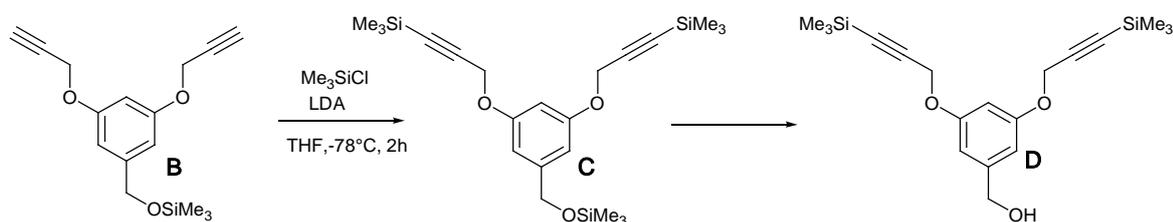
Synthesis of (3,5-Bis-prop-2-ynyloxy-benzyloxy)-trimethyl-silane (**B**)



A solution of (3,5-bis-prop-2-ynyloxy-phenyl)-methanol (**A**) (4.0 g, 18.5 mmol) and triethylamine (3.74 g, 37 mmol) in anhydrous THF (80 ml) was cooled to 0°C and stirred for 5 min. Trimethylchlorosilane (3.02 g, 27.75 mmol) was slowly added and the solution stirred at 0°C for 2 hours. The solution was then allowed to gradually reach room temperature and stirred overnight. THF was evaporated under vacuum and the crude was partitioned between water (80 ml) and dichloromethane (200 ml). The organic layer was dried over Na_2SO_4 and evaporated to dryness. The product was used for the next step without further purification. ^1H NMR spectra confirmed a quantitative derivatization.

^1H NMR (300 MHz, CDCl_3) δ (ppm): 6.60 (d, $J = 2.4$ Hz, 2H), 6.50 (t, $J = 2.4$ Hz, 1H), 4.66 (d, $J = 3.9$ Hz, 4H), 4.64 (s, 2H), 2.52 (t, $J = 3.9$ Hz, 2H). 0.16 (s, 9H). ^{13}C NMR (50 MHz, CDCl_3) δ (ppm): 158.6, 143.7, 105.9, 101, 78.6, 75.6, 64.4, 56, 0.2. MS (ESI): m/z (%) 287.2 (76), 223.2 (80), 209.2 (100), 64 (32).

Synthesis of [3,5-bis-(3-trimethylsilyl-prop-2-ynyloxy)-phenyl]-methanol (**D**)

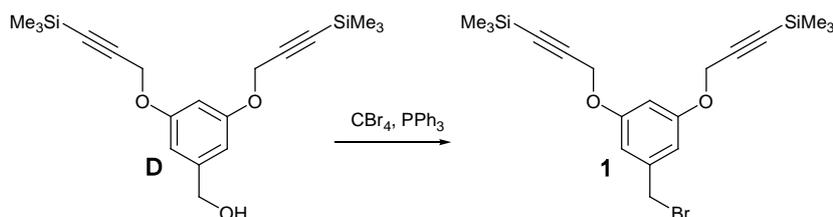


A solution of silyl ether **B** (6.0 g, 20.8 mmol) in anhydrous THF, under nitrogen atmosphere, was cooled to -78°C . Lithium diisopropylamide (1.8 M solution in THF/heptane/ethylbenzene, 45.8 mmol, 25.4 ml) was slowly added and the resulting solution was stirred at -78°C for 1 hour. TMSCl (5.65 g, 52.0 mmol) was slowly added, the mixture was stirred for additional 4 hours at -78°C then allowed to reach room temperature overnight. The mixture was cooled in an ice bath and water (10 ml) was very carefully added. After 30 minutes stirring, THF was evaporated under vacuum. The residue was partitioned between dichloromethane and water, the organic layer was then washed with brine, dried over Na_2SO_4 and evaporated. The crude mixture (containing both di-protected and mono-protected products, detectables via NMR spectra) was used for the next step without further purification.

165 ml of methanol and 3.98 g of citric acid were added to 9 grams of crude mixture obtained from the previous step. The resulting mixture was stirred for 20 minutes at r.t. TLC in dichloromethane showed a complete disappearance of the starting mixture spots and the appearance of two spots with a lower R_f value. The solvent was evaporated, the crude partitioned between water and dichloromethane. The organic layer was then washed with brine, dried over Na_2SO_4 and dichloromethane was evaporated under vacuum. The resulting mixture was purified via flash column chromatography on silica eluting with hexane:ethyl acetate 3:1 to yield 4.95 g of diprotected alkyne (pale yellow oil, $R_f = 0.42$). Total yield 66% on two steps (triple bonds protection/alcohol deprotection).

^1H NMR (300 MHz, CDCl_3) δ (ppm): 6.62 (d, $J = 2.4$ Hz, 2H), 6.53 (t, $J = 2.4$ Hz, 1H), 4.63 (s, 4H), 4.61 (s, 2H), 0.18 (s, 18H). ^{13}C NMR (50 MHz, CDCl_3) δ (ppm): 159.0, 143.3, 106.2, 101.6, 99.9, 92.8, 65.1, 56.8, -0.3 . Anal. Calcd. For $\text{C}_{19}\text{H}_{28}\text{O}_3\text{Si}_2$: C, 63.29; H, 7.83. Found C, 63.58; H, 8.11.

Synthesis of 1-bromomethyl-3,5-bis-(3-trimethylsilylprop-2-ynoxy)-benzene (**1**).

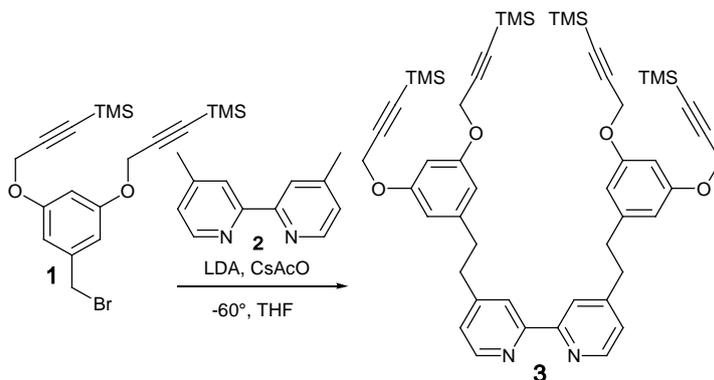


Triphenyl phosphine (4.1 g, 15.6 mmol) was added portionwise to a solution of alcohol **D** (4.5 g,

12.5 mmol) and tetrabromomethane (5.19 g, 15.6 mmol) in anhydrous THF (45 ml) under continuous stirring. The resulting solution was stirred at r.t. for 25 minutes then quenched with 10 ml of water. THF was evaporated and the product partitioned between water and dichloromethane. The organic layer was dried over Na₂SO₄ and evaporated to dryness. The crude material was purified via flash chromatography on silica gel eluting with *n*-hexane:dichloromethane 2:1 to obtain a colourless oil that solidify at fridge temperature (R_f = 0.51). Quantitative yield (5.29 g).

¹H NMR (300 MHz, CDCl₃) δ (ppm): 6.64 (d, J = 2.4 Hz, 2H), 6.53 (t, J = 2.4 Hz, 1H), 4.65 (s, 4H), 4.40 (s, 2H), 0.18 (s, 18H). ¹³C NMR (50 MHz, CDCl₃) δ (ppm): 158.5, 139.3, 108.3, 102.3, 99.4, 92.8, 56.6, 33.1, 0.45. Anal. Calcd. For C₁₉H₂₇BrO₂Si₂ : C, 53.89; H, 6.43. Found C, 53.56; H, 6.37.

Synthesis of 4,4'-bis-{2-[3,5-bis-(3-trimethylsilyl-prop-2-ynoxy)-phenyl]-ethyl}-[2,2']bipyridinyl (**3**).



Cesium acetate (0.193 g, 1.01 mmol) previously dried under vacuum, was suspended in 5.5 ml of anhydrous THF under N₂ flux. After 3 vacuum/N₂ cycles the suspension was stirred with an ultrasonic bath for 15 minutes, under nitrogen flux. Then it was stirred via a magnetic stirrer for other 10 minutes. The suspension was cooled to -60 °C (keeping magnetic stirring and N₂ flux until end of the procedure) and LDA solution (1.8 M solution in THF/heptane/ethylbenzene, 561 μl, 1.01 mmol) was added slowly, keeping internal temperature at -60 °C. The solution was stirred for 1 hour then a solution of 4,4'-dimethyl-[2,2']bipyridine (**2**) (0.077 g, 0.42 mmol) in 2 ml of anhydrous THF was slowly added. The solution was stirred at -60 °C for 1 hour and a solution of bromide **1** (0.5 g, 1.18 mmol) in 2 ml of anhydrous THF was slowly added. The mixture was stirred for additional 2 hours at -60 °C and cold-quenched with 1 ml of methanol. Then it was cautiously poured in 8 ml of a saturated NH₄Cl aqueous solution. THF was

evaporated under vacuum, dichloromethane was added and the two phases were separated. The organic layer was washed with water and brine then dried over Na₂SO₄ and evaporated. The product was purified via flash chromatography on silica, starting elution with dichloromethane then increasing polarity to dichloromethane : ethyl acetate 10:1. Pale yellow oil, 0.199 g, yield 55%.

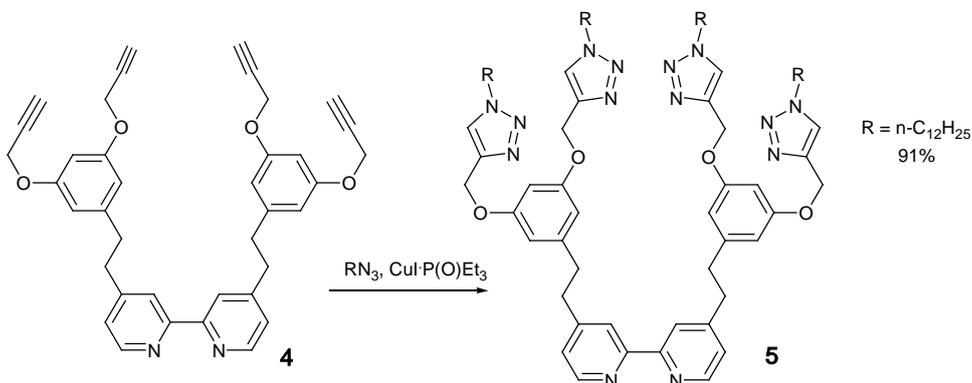
¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.57 (d, *J* = 5.6 Hz, 2H), 8.30 (d, *J* = 1.6 Hz, 2H), 7.10 (dd, *J* = 1.6 Hz, 5.6 Hz, 2H), 6.48 – 6.46 (m, 6H), 4.63 (s, 8H), 3.01 – 2.92 (m, 8H), 0.17 (s, 36H). ¹³C NMR (50 MHz, CDCl₃) δ (ppm): 158.6, 158.4, 151, 148.7, 142.8, 123.6, 120.8, 107.8, 99.8, 92.4, 56.5, 36.8, 36.7, -0.47. MS (ESI): *m/z* (%) 869.45 (M-H⁺, 100), 527.36 (8). Anal. Calcd. For C₅₀H₆₄N₂O₄Si₄ C, 69.07; H, 7.42; N, 3.22. Found C, 68.92; H, 7.36; N, 3.09.

Synthesis of 4,4'-Bis-[2-(3,5-bis-prop-2-ynyloxy-phenyl)-ethyl]-[2,2']bipyridinyl (**4**).

Dendron **3** (0.66 g, 0.76 mmol) and KF (0.35 g, 6 mmol) were dissolved in 20 ml of methanol and heated at 60°C overnight. Methanol was evaporated and the crude partitioned between water and dichloromethane. The organic phase was washed with brine, dried over Na₂SO₄ and evaporated to yield 0.44 g of a pale grey solid. Yield quantitative.

¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.56 (d, *J* = 5.6 Hz, 2H), 8.28 (d, *J* = 1.6 Hz, 2H), 7.11 (dd, *J* = 1.6 Hz, 5.6 Hz, 2H), 6.48 – 6.46 (m, 6H), 4.64 (d, *J* = 2.4 Hz, 8H), 3.01 - 2.92 (m, 8H), 2.51 (t, *J* = 2.4 Hz, 4H). ¹³C NMR (50 MHz, CDCl₃) δ (ppm): 158.7, 156.2, 151.4, 149.1, 143.4, 124, 121.2, 108.2, 100.2, 78.5, 75.6, 55.9, 36.9, 36.8. MS (ESI): *m/z* (%) 603.27 (M-Na⁺, 5), 581.36 (M-H⁺, 100). Anal. Calcd. For C₃₈H₃₂N₂O₄: C, 78.60; H, 5.55; N, 4.82. Found C, 78.54; H, 5.33; N, 4.70

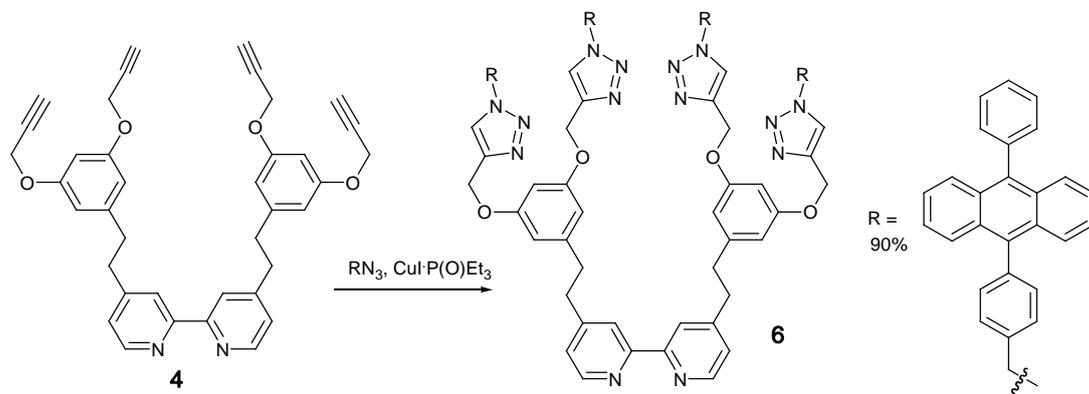
Synthesis of 4,4'-bis-{2-[3,5-bis-(1-dodecyl-1H-[1,2,3]triazol-4-ylmethoxy)-phenyl]-ethyl}-[2,2']bipyridine (**5**)



Dodecylazide (50 mg, 0.237 mmol), dendron **4** (31 mg, 0.054 mmol) and CuP(OEt)₃ (8.45 mg, 0.0237 mmol) were dissolved in 1.5 ml of THF and irradiated with microwaves for 15 minutes (nominal power 300 W, maximum temperature 50°C). THF was evaporated under vacuum, The crude material was dissolved in dichloromethane and washed with concentrated ammonia (3x10ml), water and brine. The organic layer was dried over Na₂SO₄ and evaporated. The crude mixture was purified via flash column chromatography on silica gel, eluting with dichloromethane:methanol 20:1. Pale grey solid, 70 mg, yield 91%.

¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.55 (d, J = 5.2 Hz, 2H), 8.27 (d, J = 1.6 Hz, 2H), 7.59 (s, 4H), 7.10 (dd, J = 1.6 Hz, 5.2 Hz, 2H), 6.52 (t, J = 2.4 Hz, 2H), 6.48 (d, J = 2.4 Hz, 4H), 5.16 (s, 8H), 4.34 (t, J = 7.2 Hz, 8H), 2.99 – 2.92 (m, 8H), 1.90 (m, 8H), 1.34 – 1.23 (m, 72 H), 0.87 (t, J = 6.8 Hz, 12H). ¹³C NMR (50 MHz, CDCl₃) δ (ppm): 165.6, 159.4, 156, 151.3, 148.9, 143.9, 143.8, 123.9, 122.4, 121.2, 107.9, 99.8, 62.3, 50.5, 37.1, 32, 30.4, 29.7, 29.6, 29.5, 29.4, 29.1, 26.7, 22.8, 14.3. MS (ESI): m/z (%) 1464.91 (M-K⁺, 5), 1449 (M-Na⁺, 8), 1426 (M-H⁺, 100), 1176.82 (7), 724.64 (M-Na⁺-H⁺, double charged, 8), 714.09 (M-2H⁺, double charged, 18). Anal. Calcd. For C₈₆H₁₃₂N₁₄O₄: C, 72.43; H, 9.33; N, 13.75. Found C, 72.27; H, 9.31; N, 13.38.

Dendrimeric ligand **6**



A solution of (9-(4-Azidomethyl-phenyl)-10-phenyl-anthracene)⁴ (92 mg, 0.237 mmol), dendron **4** (31 mg, 0.054 mmol) and $CuIP(OEt)_3$ (8.45 mg, 0.0237 mmol) in 1.5 ml of THF was irradiated with microwaves for 15 minutes (nominal power 300 W, maximum temperature 50°C). THF was evaporated under vacuum. The residue was dissolved in dichloromethane and washed with concentrated ammonia (3x10ml), water and brine. The organic layer was dried over Na_2SO_4 and evaporated. The crude mixture was purified via flash column chromatography on silica gel, eluting with dichloromethane:methanol 20:1 ($R_f = 0.55$). Pale grey waxy solid, 103 mg, yield 90%.

¹H NMR (300 MHz, $CDCl_3$): δ 8.54 (d, $J = 3.6$ Hz, 2H), 8.28 (s, 2H), 7.80 (s, 4H), 7.80-7.20 (m, 68H), 7.08 (d, $J = 3.2$ Hz, 2H), 6.58 (s, 2H), 6.50 (s, 4H), 5.69 (s, 8H), 5.22 (s, 8H), 2.96 (bs, 8H). ¹³C NMR (75 MHz, $CDCl_3$): δ 159.4 (s, 4C), 151.3 (s, 2C), 149.0 (s, 2C), 144.5 (d, 2C), 143.5 (s, 2C), 139.7 (s, 4C), 138.8 (s, 4C), 137.4 (s, 4C), 135.8 (s, 4C), 133.8 (s, 4C), 132.0 (s, 8C), 131.2 (s, 8C), 129.8 (d, 8C), 129.7 (d, 8C), 128.4 (d, 16C), 128.1 (d, 8C), 127.5 (d, 4C), 127.0 (d, 8C), 126.6 (d, 8C), 125.2 (d, 8C), 125.1 (d, 8C), 124.0 (d, 2C), 123.0 (d, 2C), 108.2 (d, 4C), 100.2 (d, 2C), 62.35 (t, 4C), 54.2 (t, 4C), 37.2 (t, 2C), 36.9 (t, 2C). ESI MS $M+2H^+$ 1061.6; Elemental analysis calculated for $C_{146}H_{108}N_{14}O_4$ (MW 2122.51): C, 82.62; H, 5.13; N, 9.24. Found: C, 82.63; H, 5.09; N, 8.86.

Synthesis of complex **7**

Compound **6** (90 mg, 0.042 mmol) and $[Ru(bpy)_2Cl_2] \cdot 2H_2O$ (14.4 mg, 0.027 mmol) were refluxed in 2 ml of DMF overnight. The solution was then diluted with water (10 ml) and an excess of NH_4PF_6 (83 mg, 0.5 mmol) was added. The precipitate was collected and purified via

column chromatography on neutral aluminium oxide starting elution with chloroform then increasing polarity (CHCl₃:MeOH 30:1, 20:1, 10:1) to obtain 20 mg of an orange solid.

¹H NMR (300 MHz, CDCl₃): δ 8.40-7.00 (m, 124 H), 6.45 (s, 2H), 6.50 (s, 4H), 5.60 (s, 8H), 5.08 (s, 8H), 2.96 (bs, 8H).

ESI MS : 1268.09 (M²⁺).

Efficiency of quenching

The rates of the quenching processes can be evaluated by the following equation:

$$k_q = 1/\tau - 1/\tau^0 = 1/\tau^0 (\Phi^0/\Phi - 1)$$

where τ , τ^0 and Φ , Φ^0 are the excited state lifetimes and emission quantum yields of the chromophore inserted in the dendritic structure **7** and of the model compound, respectively (see Table 1). The corresponding efficiency (η_q) can be calculated as follows:

$$\eta_q = k_q \times \tau$$

In the case of DPA in the dendritic structure, the corresponding lifetime is below the instrument resolution and the k_q can be estimated by a comparison of the emission quantum yield taking into account the light absorbed by the different chromophoric units. To estimate the quenching efficiency a value of τ is necessary, so that we assumed that quenching of lifetime and emission quantum yield is the same, i.e. $\Phi/\Phi^0 = \tau/\tau^0$, as in the case of the [Ru(bpy)₃]²⁺ chromophore.

Up-converted emission experiments

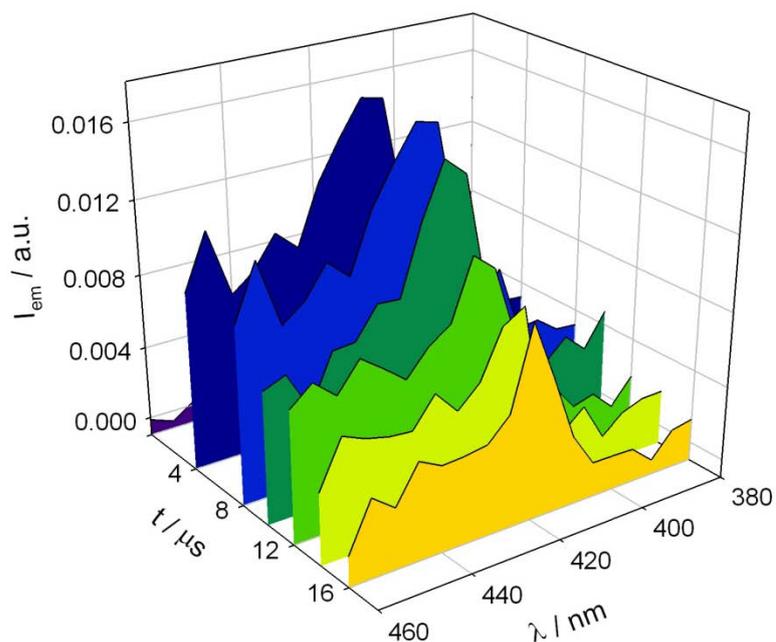


Figure S1. Emission spectra as a function of delay from the excitation of a 4.2×10^{-5} M solution of **7** in C_2H_5OH/CH_2Cl_2 1:1 (v/v) rigid matrix at 77 K. $\lambda_{ex} = 532$ nm.

- ¹ L. Prodi and A. Credi, From observed to corrected luminescence intensity of solution systems: an easy-to-apply correction method for standard spectrofluorimeters, *Spectrochimica Acta A*, 1998, 54, 159.
- ² J. N. Demas and G. A. Crosby, Measurement of photoluminescence quantum yields. A review, *J. Phys. Chem.*, 1971, 75, 991.
- ³ M. Montalti, A. Credi, L. Prodi, M. T. Gandolfi, *Handbook of Photochemistry*, 3rd ed., ch.7, CRC Press, Boca Raton, FL, USA, 2006.
- ⁴ For azide see : (a) W. Fudickar, T. Linker, *Chem. Eur. J.* **2006**, 12, 9276-9283. (b) A. S. Thompson, G. R. Humphrey, A. M. DeMarco, D. J. Mathre, E. J. J. Grabowski, *J. Org. Chem.* **1993**, 58, 5886-5888.