

Photoswitchable metal coordinating tweezers operated by light-harvesting dendrimers

Enrico Marchi,^a Massimo Baroncini,^a Giacomo Bergamini,^a Jeroen Van Heyst,^b Fritz Vögtle^b and Paola Ceroni^{a*}

^aDepartment of Chemistry “G. Ciamician”, University of Bologna, via Selmi 2, 40126 Bologna – Italy, E-mail: paola.ceroni@unibo.it

^bKekulé-Institut für Organische Chemie und Biochemie, Universität Bonn, Gerhard-Domagk Strasse 1, D-53121 Bonn, Germany

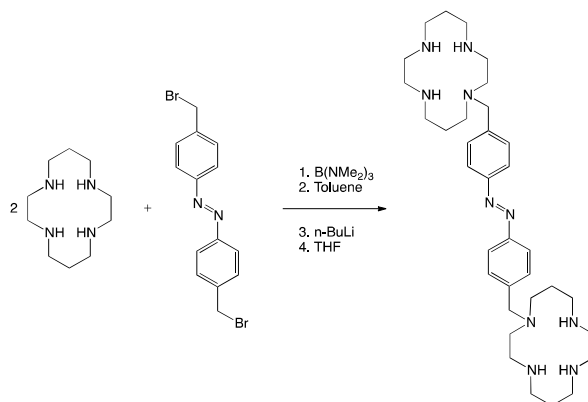
Supporting Information

Materials and Characterization Methods.

Compound *t*-Azo,¹ bis(4-bromomethylphenyl)diazene² and 3,5-bis(2'-naphthalenylmethoxy)benzylbromide³ were synthesized according to previously published procedures. Commercially available compounds, including 2-(bromomethyl)naphthalene and 1,4,8,11-tetraazacyclotetradecane, were reagent grade quality and were used without further purification. Solvents were dried according to literature procedures. The ¹H and ¹³C NMR spectra were recorded at 298 K in CD₃CN with a Varian Mercury 400 spectrometer with the deuterated solvent as the lock and the residual solvent as the internal standard. All chemical shifts are quoted using the δ scale and all coupling constants (J) are expressed in Hertz (Hz).

Synthesis.

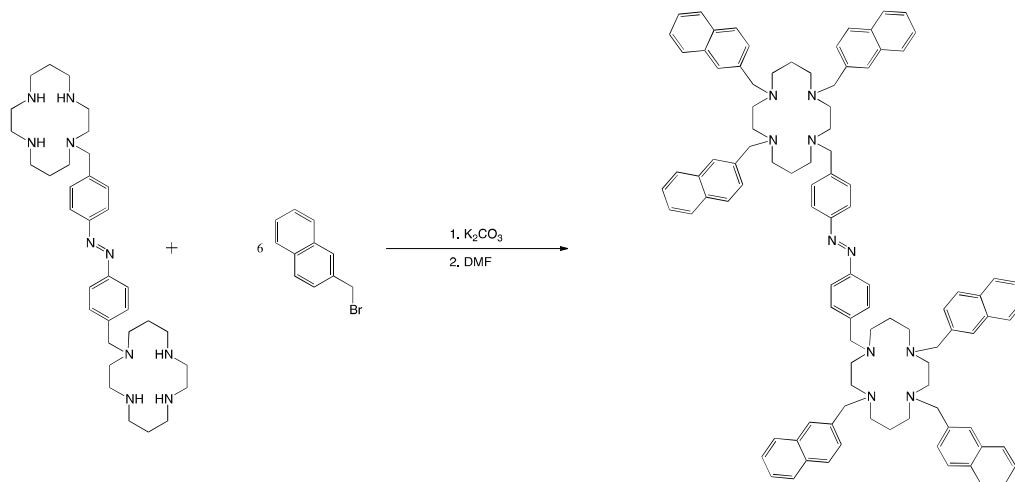
1,1'-[bis(methylphenyl)diazene]bis(1,4,8,11-tetraazacyclotetradecane), C(*t*-Azo)



200 mg (1.0 mmol) of 1,4,8,11-tetraazacyclotetradecane was taken up in 20 ml of toluene and put under an argon atmosphere. 0.175 ml (143 mg, 1.0 mmol) of tris-(dimethylamino)borane was added and the resulting mixture was stirred for 3 hours at reflux. The solvent was removed under vacuum and the resulting solid was taken up in 20 ml of dry THF and cooled to -40°C. 0.4 ml (2.5M, 1.0 mmol) of *t*-butyl lithium was added and the resulting mixture stirred for 15 minutes. 184 mg (0.5 mmol) of bis(4-bromomethylphenyl)diazene was added and the resulting

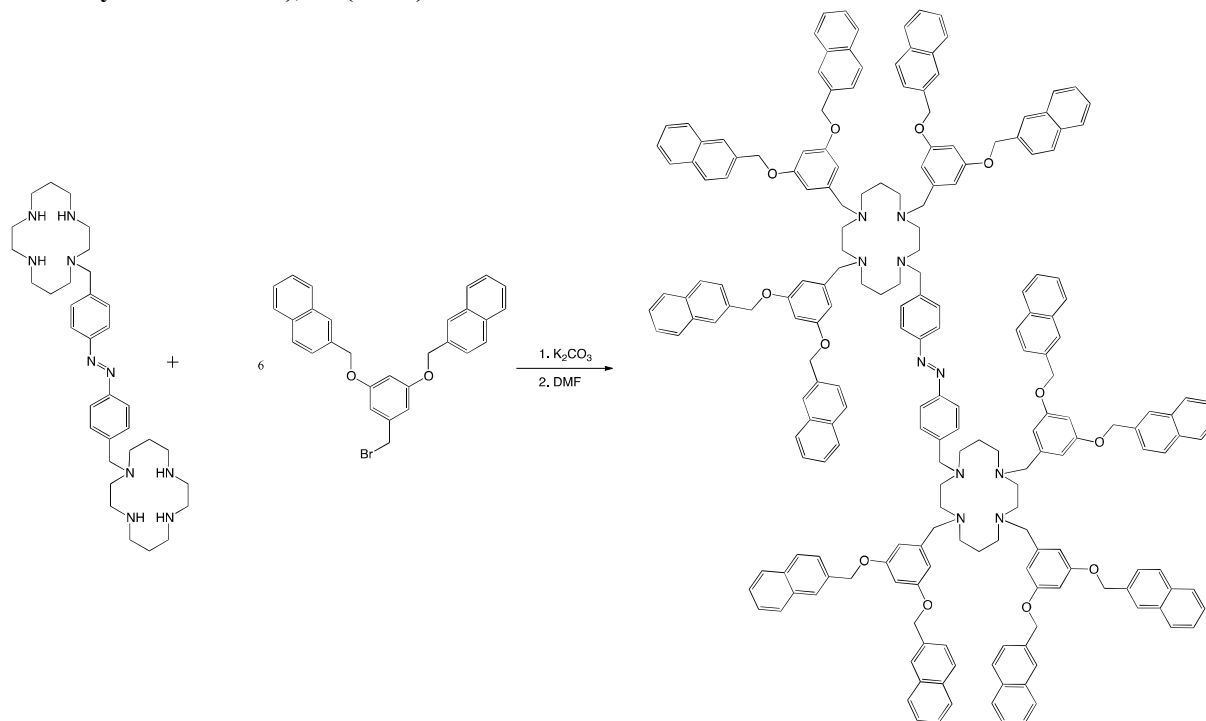
mixture was allowed to heat to RT and stirred for 2 hours. Water was then added and the mixture was brought to pH 14 by addition of a 4M solution of NaOH. The organic solvent was removed under vacuum and the residue extracted with DCM. The organic phase was dried over Na₂SO₄ and the solvent removed under vacuum to afford 360 mg (60% yield) of the title compound. ¹H-NMR (400 MHz, CDCl₃, 25°C) δ (ppm): 1.69-1.73 (m, 8H), 2.42-2.84 (m, 32H), 3.63 (s, 4H), 7.48 (d, 4H, J= 8.36 Hz), 7.83 (d, 4H, J=7.37 Hz). ¹³C-NMR (100.6 MHz, CDCl₃, 25°C) δ (ppm): 26.4, 47.5, 49.3, 49.4, 50.7, 50.8, 53.5, 55.0, 58.8, 122.6, 129.7, 142.3, 151.8. MS (HR-ESI): expected 606.4846, found 607.4892 [M+H]⁺.

1,1'-[bis(methylphenyl)diazene]-4,4',8,8',11,11'-hexakis(methylnaphthyl)bis(1,4,8,11-tetrazacyclotetradecane), G0(*t*-Azo)



57.1 mg (0.09 mmol) of **C(*t*-Azo)** were taken up in 10 ml of dry DMF and 156 mg (1.13 mmol) of K₂CO₃ were added. The resulting mixture was stirred for 10 minutes at RT under an argon atmosphere. Then 143.7 mg (0.65 mmol) of 2-(bromomethyl)naphthalene dissolved in 5 ml of dry DMF was added dropwise. The resulting mixture was stirred at RT overnight. The solvent was removed under vacuum and the residue was taken up in CH₂Cl₂. The organic phase was extracted with saturated NaHCO₃, water, dried over Na₂SO₄ and the solvent removed under vacuum. The product was purified by column chromatography (SiO₂, CH₂Cl₂/MeOH, 10:1) to yield the title compound as a pale yellow foam (130 mg, 46 %). ¹H-NMR (400 MHz, CDCl₃, 25°C) δ (ppm): 1.85 (brm, 8H), 2.51-2.59 (m, 32H), 3.58 (m, 16H), 7.39 (m, 12H), 7.43-7.52 (m, 8H), 7.63-7.78 (m, 22H). ¹³C-NMR (100.6 MHz, CDCl₃, 25°C) δ (ppm): 26.2, 46.8, 49.7, 58.9, 64.7, 65.3, 71.4, 122.2, 125.1, 127.1, 127.6, 128.5, 129.2, 133.8, 142.5, 151.4. MS (HR-ESI): expected 3021.4632, found 3022.3297 [M+H]⁺.

1,1'-[bis(methylphenyl)diazene]-4,4',8,8',11,11'-hexakis[3,5-bis(2'-oxymethylnaphthyl)benzyl]bis(1,4,8,11-tetrazacyclotetradecane), G1(*t*-Azo)



57.1 mg (0.09 mmol) of **G0(*t*-Azo)** were taken up in 10 ml of dry DMF and 156 mg (1.13 mmol) of K₂CO₃ were added. The resulting mixture was stirred for 10 minutes at RT under an argon atmosphere. Then 300 mg (0.621 mmol) of 3,5-bis(2'-naphthalenylmethoxy)benzyl bromide dissolved in 5 ml of dry DMF was added dropwise. The resulting mixture was stirred at RT for 4 days. The solvent was removed under vacuum and the residue was taken up in CH₂Cl₂. The organic phase was extracted with saturated NaHCO₃, water, dried over Na₂SO₄ and the solvent removed under vacuum. The product was purified by column chromatography (SiO₂, CH₂Cl₂/MeOH, 10:1) to yield the title compound as an orange foam (130 mg, 46 %). ¹H-NMR (400 MHz, CD₂Cl₂, 25° C) δ (ppm): 1.78-1.80 (m, 8H), 2.51-2.59 (m, 32H), 3.38 (br s, 16H), 4.94-5.00 (m, 24H), 6.48-6.73 (m, 8H), 7.40-7.44 (m, 18H), 7.73-7.78 (m, 84H). ¹³C-NMR (100.6 MHz, CDCl₃, 25°C) δ (ppm): 26.2, 46.8, 49.7, 58.9, 64.7, 65.3, 71.4, 122.2, 125.1, 127.1, 127.6, 128.5, 129.2, 133.8, 142.5, 151.4. MS (HR-ESI): expected 3021.4632, found 3022.3297 [M+H]⁺.

Photophysical experiments. The experiments were carried out in air-equilibrated CH₃CN/CH₂Cl₂ 1:1 (v/v) solution at 298 K. UV-Vis absorption spectra were recorded with a Perkin Elmer λ40 spectrophotometer, using quartz cells with pathlength of 1.0 or 5.0 cm. Fluorescence spectra were obtained with a Perkin Elmer LS-50 spectrofluorimeter, equipped with a Hamamatsu R928 phototube. Fluorescence quantum yields were measured following the method of Demas and Crosby⁴ (standard used: naphthalene in aerated cyclohexane solution).⁵ Global fitting of absorption and emission spectra has been performed by Specfit software.⁶ The estimated experimental errors are: 2 nm on the band maximum, 5% on the molar absorption coefficient and log *K* values, 10% on the fluorescence quantum yield.

Photochemical experiments. Photochemical experiments at 365 and 436 nm were performed by a medium pressure mercury lamp, an interference filter (Oriel) was used to select a narrow spectral range with λ_{max} = 365 and 436 nm. Photochemical experiments at 275 nm were performed using a 150 W continuous xenon arc lamp and a monochromator. The irradiated solution was contained in a spectrophotometric cell and stirred continuously. The intensity of the incident light was measured by the ferrioxalate actinometer.⁷ The photoisomerisation quantum yield (Φ_{t→c} or Φ_{c→t}) was calculated by extrapolation to zero time of the apparent quantum yield values obtained for short

irradiation periods. The observed decrease of the apparent quantum yield versus time of irradiation (Figure 2, inset) is due to the increasing percentage of light absorbed by the *cis* isomer at the irradiation wavelength. By extrapolating at time zero, this effect is minimized. The relative amounts of *cis* and *trans* isomers during photochemical experiments has been calculated by assuming for all the investigated compounds the same value of the molar absorption coefficient of *cis*-azobenzene in the $n\pi^*$ band.

The estimated experimental errors are: 10% on the photoreaction quantum yield, 5% on the composition of the photostationary state.

Table S1. Most relevant photophysical data of the investigated dendrimers in CH₂Cl₂/CH₃CN 1:1 (v/v) solution at 298 K.

	absorption		emission	
	λ / nm	ϵ / 10 ³ M ⁻¹ cm ⁻¹	λ / nm	$\Phi_{\text{em}}/10^{-3}$ [a]
G0(<i>t</i>-Azo)	276	26.6	335	0.6
	336	21	470	
G0(<i>c</i>-Azo)^[b]	276	27	335	0.6
	440	1.4	470	
G1(<i>t</i>-Azo)	276	75	335	1.1
	336	21	400 ^{sh}	
G1(<i>c</i>-Azo)^[b]	276	74.6	335	2.1
	440	1.6	400 ^{sh}	

[a] A correction for the percentage of light absorbed by azobenzene in **G0(*t*-Azo)** and **G1(*t*-Azo)** has been performed. [b] The molar absorption coefficients are estimated using *c*-Azo as model compound.

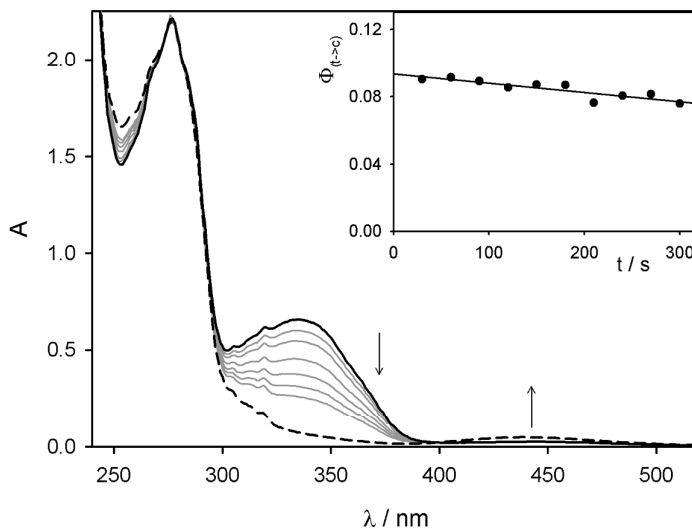


Figure S1. Isomerization of a 3.1×10^{-5} M solution of **G1(*t*-Azo)** (thick solid line) in CH₃CN/CH₂Cl₂ 1:1 (v/v) upon irradiation at 365 nm at 298 K: the photostationary state is represented by the thick dashed line. Inset shows the apparent $t \rightarrow c$ photoreaction quantum yield ($\Phi_{t \rightarrow c}$) vs time.

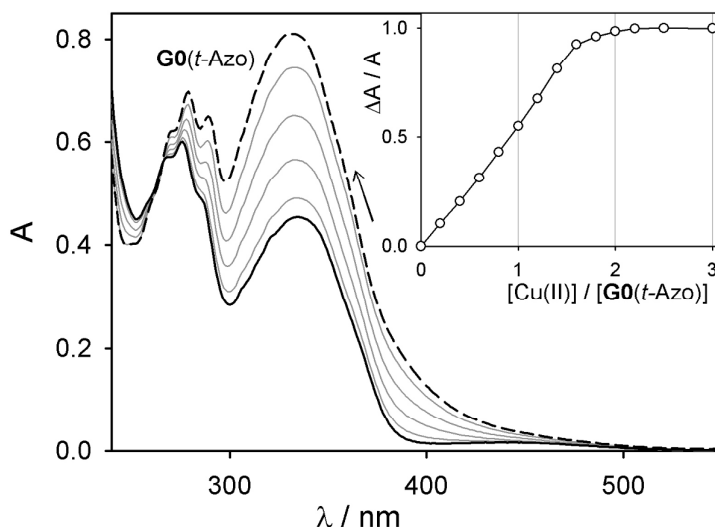


Figure S2. Absorption spectra of a 2.2×10^{-5} M solution of **G0(t-Azo)** in $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$ 1:1 (v/v) during the titration with $\text{Cu}(\text{CF}_3\text{SO}_3)_2$: 0 eq. (thick solid line), 3 eq. (thick dashed line). Inset shows the normalized absorption changes at 335 nm.

The association constants derived by global fitting of the spectra reported in Figure S2 are: $K_1 = 2 \times 10^7 \text{ M}^{-1}$, $K_2 = 1 \times 10^8 \text{ M}^{-1}$.

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⁴ J. N. Demas and G. A. Crosby, *J. Phys. Chem.*, 1971, **75**, 991-1024.

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