Supporting Information

Light-triggered Self-assembly of Triarylamine-based Nanospheres

Emilie Moulin,[a] Frédéric Niess,[a] Gad Fuks,[a] Nicolas Jouault,[b] Eric Buhler,[b] and Nicolas Giuseppone[a*]

[a] *SAMS research group – University of Strasbourg, Institut Charles Sadron, CNRS, 23 rue du Loess, BP 84087, 67034 Strasbourg Cedex 2, France*

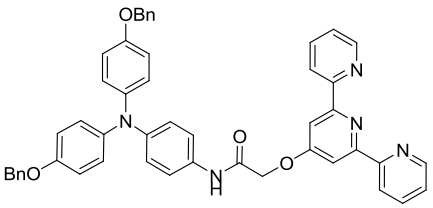
Fax: (+) 33 (0)3 88 41 40 99

E-mail : giuseppone@unistra.fr

[b] *Matière et Systèmes Complexes (MSC) Laboratory, University of Paris Diderot – Paris VII, UMR 7057, Bâtiment Condorcet, 75205 Paris Cedex 13, France*

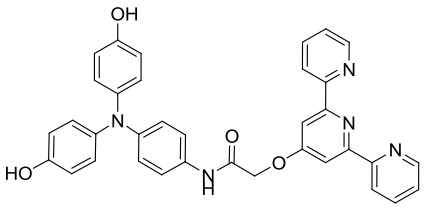
Synthetic procedures and products characterisation

All *reagents and solvents* were purchased at the highest commercial quality and used without further purification unless otherwise noted. Dry solvents were obtained using a double column SolvTech purification system. Yields are not optimized and refer to single reaction experiment. Yields refer to purified spectroscopically (^{1}H NMR) homogeneous materials. *Thin Layer Chromatographies* were performed with TLC silica plastic sheets (Polygram SIL G/UV$_{254}$, Macherey-Nagel) or TLC alox plastic sheets (Polygram Alox N/UV$_{254}$, Macherey-Nagel). In most cases, irradiation using a *Bioblock VL-4C* UV-Lamp (6 W, 254 nm and/or 365 nm) as well as 10% ethanolic phosphomolybdic acid and Ce-molybdate stainings were used for visualization. *Preparative Adsorption Flash Column Chromatographies* were performed using silica gel (Geduran, silica gel 60 (230 – 400 mesh, 40 – 63 µm, Merck)) and aluminium oxide 90 (Merck; 70 - 230 mesh, standardized activity II). *Preparative High Pressure Liquid Chromatograpy* was performed using a Dynamax SD-200 / Merck system equipped with a reverse phase (C18) column (water / methanol gradients) and with a UV detector. *Ultra Performance Liquid Chromatographies coupled to Mass Spectroscopy* (UPLC-MS) were carried out on a *Waters Acquity UPLC-SQD* apparatus equipped with a PDA detector (190-500 nm, 80Hz), using a reverse phase column (Waters, BEH C18 1.7 µm, 2.1mm x 50 mm), and the MassLynx 4.1 – XP software. *^{1}H NMR spectra* were recorded on a *Bruker Avance 400* spectrometer at 400 MHz and ^{13}C spectra at 100 MHz in $CDCl_3$ and MeOD at 25°C. The spectra were internally referenced to the residual proton solvent signal. For ^{1}H NMR assignments, the chemical shifts are given in ppm. Coupling constants *J* are listed in Hz. The following notation is used for the ^{1}H NMR spectral splitting patterns: singlet (s), doublet (d), triplet (t), multiplet (m), large (l).

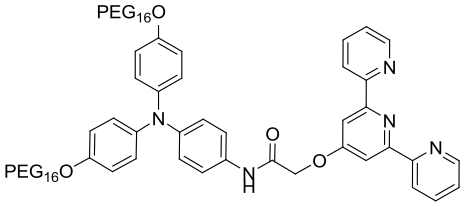


A suspension of compound **1**[1] (621 mg, 1.13 mmol), terpyridone[2] (282 mg, 1.13 mmol) and potassium carbonate (467 mg, 3.39 mmol) in DMF (113 mL) was stirred overnight at 60°C. After cooling down to room temperature, the mixture was filtered to remove potassium carbonate. The reaction mixture

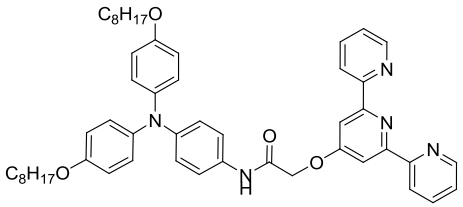
was dissolved with CH_2Cl_2 (100 mL), extracted with $NH_4Cl_{sat.}$ (2*80 mL) and brine (50 mL), dried over $MgSO_4$ and concentrated under reduced pressure. Further purification by column chromatography (Al_2O_3, Cyclohexane → Cyclohexane/EtOAc: 1/5) afforded compound **2** as a brown oil (647 mg, 75%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25°C) δ = 8.71 (d, ^3J = 4.7Hz, 2H), 8.63 (d, ^3J = 7.9Hz, 2H), 8.22 (s, 1H), 8.14 (s, 2H), 7.87 (ddd, J = 7.7, 7.7, 1.8Hz, 2H), 7.46-7.31 (m, 14H), 7.03 (d, ^3J = 9.0Hz, 4H), 6.97 (d, ^3J = 8.9Hz, 2H), 6.90 (d, ^3J = 9.0Hz, 4H), 5.04 (s, 4H), 4.85 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, 25°C) δ = 165.02, 164.74, 157.65, 155.45, 154.85, 149.11, 145.80, 141.28, 137.07, 136.90, 129.97, 128.55, 127.93, 127.51, 125.98, 124.15, 121.94, 121.37, 121.34, 115.61, 107.21, 70.31; ESI-MS: m/z calculated for $C_{49}H_{39}N_5O_4$ $[M+H]^+$ 762.30; found 762.55.



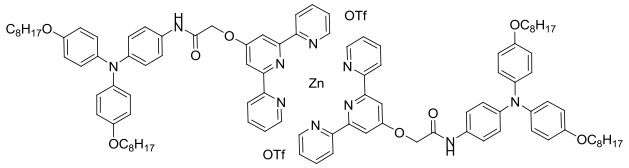
In a typical experimental setup, 26 mg of compound **2** was dissolved in 3.4 mL EtOAc:MeOH (1:1). A H-Cube continuous flow reactor was used for the hydrogenation. The flow rate was set with the HPLC pump to 1 mL/min. The hydrogen pressure was set to 40 bars, the temperature to 80°C and a cartridge containing 10% Pd/C was used. After the reaction, the sample was collected and evaporated to give product **3**, which was pure enough to be used as such in the next step.[3] ^{1}H NMR (CD_3OD, 400 MHz, 25°C) δ = 8.65 (d, ^3J = 4.1Hz, 2H), 8.58 (d, ^3J = 8.0Hz, 2H), 8.04 (s, 2H), 7.96 (ddd, J = 7.8, 7.7, 1.8Hz, 2H), 7.44 (ddd, J = 7.5, 4.8, 1.2Hz, 2H), 7.37 (d, ^3J = 9.0Hz, 2H), 6.88 (d, ^3J = 8.8Hz, 4H), 6.80 (d, ^3J = 9.0Hz, 2H), 6.71 (d, ^3J = 8.9Hz, 4H), 4.90 (s, 2H); ^{13}C NMR (CD_3OD, 100 MHz, 25°C) δ = 167.73, 158.71, 157.03, 154.83, 150.22, 147.97, 141.60, 138.88, 131.27, 127.80, 125.74, 123.41, 123.12, 121.60, 117.19, 108.79, 68.34; ESI-MS: m/z calculated for $C_{35}H_{27}N_5O_4$ $[M+H]^+$ 582.21; found 582.38.



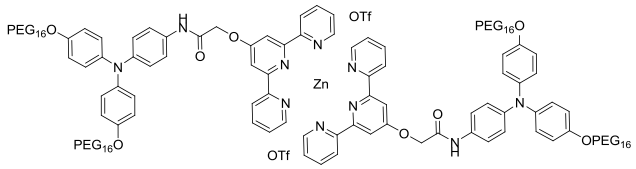
A suspension of compound **3** (0.26 mmol), $PEG_{16}OTs$[4] (468 mg, 0.52 mmol) and potassium carbonate (145 mg, 1.05 mmol) in acetone (22 mL) was stirred for one week at reflux. After cooling down to room temperature, the mixture was filtered to remove potassium carbonate and the resulting solution was concentrated under reduced pressure. Further purification by reverse phase preparative HPLC afforded compound **4** as an orange oil (50.5 mg, 10% over 2 steps). ^{1}H NMR ($CDCl_3$, 400 MHz, 25°C) δ = 8.68 (d, ^3J = 4.8Hz, 2H), 8.62 (d, ^3J = 7.9Hz, 2H), 8.22 (s, 1H), 8.12 (s, 2H), 7.86 (ddd, J = 7.7, 7.7, 1.8Hz, 2H), 7.40 (d, ^3J = 9.0Hz, 2H), 7.35 (ddd, J = 7.5, 4.8, 1.1Hz, 2H), 6.98 (d, ^3J = 9.0Hz, 4H), 6.92 (d, ^3J = 9.0Hz, 2H), 6.80 (d, ^3J = 9.0Hz, 4H), 4.84 (s, 2H), 4.08 (t, ^3J = 4.9Hz, 4H), 3.83 (t, ^3J = 4.9Hz, 4H), 3.72-3.52 (m, 120H), 3.36 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz, 25°C) δ = 165.03, 164.71, 157.63, 155.42, 154.74, 149.08, 145.77, 141.16, 136.88, 129.90, 125.89, 124.12, 121.81, 121.32, 121.30, 115.35, 107.19, 77.21, 71.86, 70.74, 70.56, 70.49, 70.45, 69.71, 67.62, 66.89, 58.97; ESI-MS: m/z calculated for $C_{101}H_{159}N_5O_{36}$ $[M+H_3O+H]^{2+}$ 1019.54; found 1018.97.



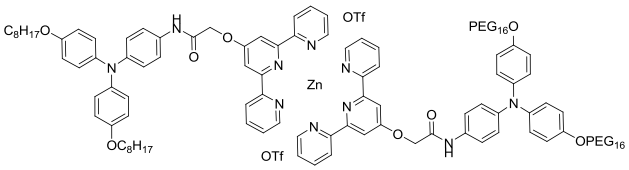
A suspension of compound **5**[1] (226 mg, 0.38 mmol), terpyridone[2] (95 mg, 0.38 mmol) and potassium carbonate (158 mg, 1.14 mmol) in DMF (38 mL) was stirred overnight at 60°C. After cooling down to room temperature, the mixture was filtered to remove potassium carbonate. The reaction mixture was dissolved with CH_2Cl_2 (50 mL), extracted with $NH_4Cl_{\ sat.}$ (2*50 mL) and brine (40 mL), dried over $MgSO_4$ and concentrated under reduced pressure. Further purification by column chromatography (Al_2O_3, Cyclohexane → Cyclohexane/EtOAc: 1/5) afforded compound **6** as a brown solid (250 mg, 82%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25°C) δ = 8.70 (d, ^3J = 4.6Hz, 2H), 8.63 (d, ^3J = 7.9Hz, 2H), 8.23 (s, 1H), 8.14 (s, 2H), 7.86 (brddd, J = 7.8, 7.7, 1.8Hz, 2H), 7.41 (d, ^3J = 8.8Hz, 2H), 7.35 (dd, J = 7.3, 4.9Hz, 2H), 7.01 (d, ^3J = 8.6Hz, 4H), 6.94 (d, ^3J = 8.8Hz, 2H), 6.80 (d, ^3J = 8.8Hz, 4H), 4.85 (s, 2H), 3.92 (t, ^3J = 6.5Hz, 4H), 1.77 (tt, ^3J = 7.3, 6.6Hz, 4H), 1.49-1.42 (m, 4H), 1.37-1.24 (m, 16H), 0.89 (t, ^3J = 6.5Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz, 25°C) δ = 165.25, 164.71, 157.39, 155.23 (x2), 149.05, 145.99, 140.88, 137.05, 129.73, 126.09, 124.25, 121.55, 121.45, 121.36, 115.22, 107.37, 68.25, 31.80, 29.35, 29.23, 26.06, 22.64, 14.08; ESI-MS: m/z calculated for $C_{51}H_{59}N_5O_4$ $[M+H]^+$ 806.46; found 806.39.



A solution of zinc triflate (1 mg, 2.8 µmol) in deuterated methanol (50 µL) was added to a solution of compound **6** (4.4 mg, 5.5 µmol) in deuterated chloroform (400 µL) and the resulting solution was shaken for homogeneity. ^{1}H NMR ($CDCl_3$, 400 MHz, 25°C) δ = 9.72 (s, 2H), 8.59 (d, ^3J = 8.1Hz, 4H), 8.34 (s, 4H), 8.04 (ddd, J = 7.8, 7.8, 1.6Hz, 4H), 7.66 (d, ^3J = 4.7Hz, 4H), 7.46 (d, ^3J = 7.2Hz, 4H), 7.33 (dd, J = 7.2, 5.4Hz, 4H), 6.90 (brm, 12H), 6.73 (d, ^3J = 8.4Hz, 8H), 5.27 (s, 4H), 3.86 (brs, 8H), 1.70 (tt, ^3J = 7.4, 6.8Hz, 8H), 1.42-1.34 (m, 8H), 1.30-1.19 (m, 32H), 0.82 (t, ^3J = 6.8Hz, 12H); ESI-MS: m/z calculated for $C_{103}H_{118}N_{10}O_{11}F_3SZn$ $[M]^+$ 1825.797; found 1826.161.

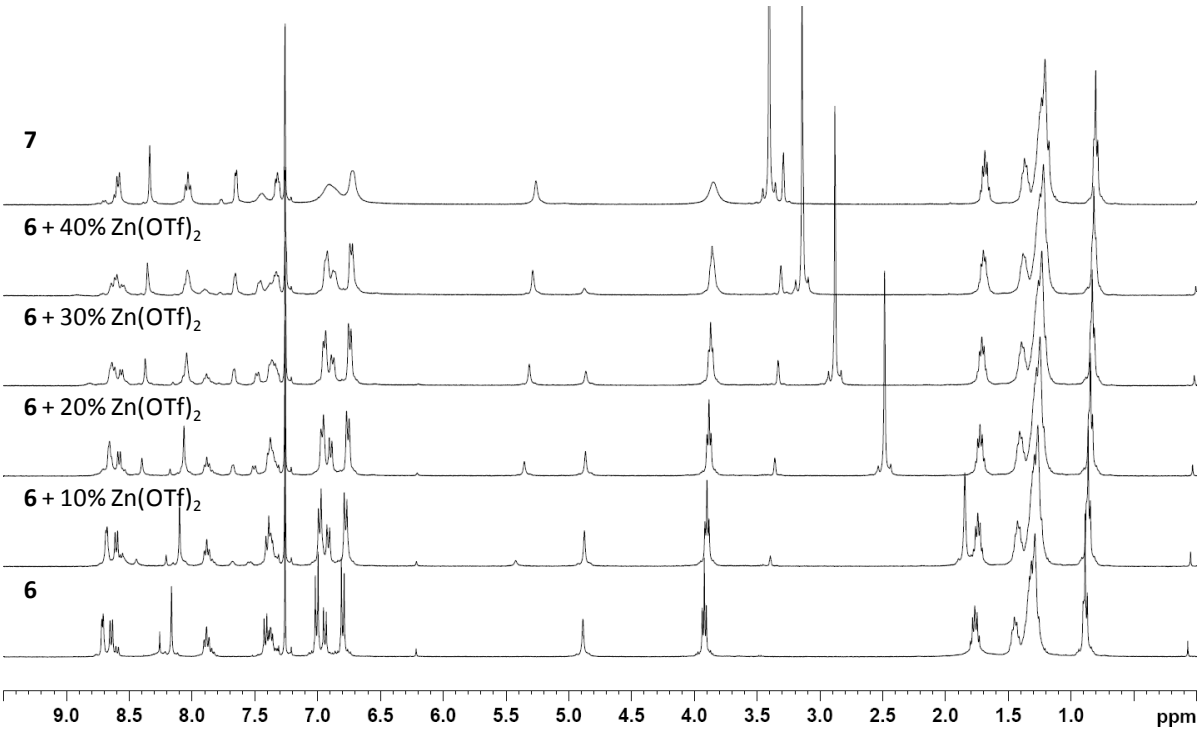


A solution of zinc triflate (1 mg, 2.8 µmol) in deuterated methanol (50 µL) was added to a solution of compound **4** (11.1 mg, 5.5 µmol) in deuterated chloroform (450 µL) and the resulting solution was shaken for homogeneity. ^{1}H NMR ($CDCl_3$, 400 MHz, 25°C) δ = 9.86 (s, 2H), 8.63 (d, ^3J = 7.8Hz, 4H), 8.38 (s, 4H), 8.04 (dd, J = 7.7, 7.7Hz, 4H), 7.65 (d, ^3J = 4.3Hz, 4H), 7.48 (d, ^3J = 8.3Hz, 4H), 7.35 (dd, J = 6.5, 5.5Hz, 4H), 6.91 (d, ^3J = 8.9Hz, 8H), 6.86 (d, ^3J = 8.9Hz, 4H), 6.74 (d, ^3J = 9.0Hz, 8H), 5.29 (s, 4H), 4.02 (t, ^3J = 4.8Hz, 8H), 3.77 (t, ^3J = 4.8Hz, 8H), 3.66-3.46 (m, 240H), 3.30 (s, 12H).



A solution of zinc triflate (1 mg, 2.8 µmol) in deuterated methanol (50 µL) was added to a solution of compound **4** (5.6 mg, 2.8 µmol) in deuterated chloroform (300 µL) and the resulting solution was shaken for homogeneity. ^{1}H NMR of the mixture revealed full complexation of zinc to the terpyridine. Then, a solution of compound **6** (2.2 mg, 2.8 µmol) in deuterated chloroform (100 µL) was added to the solution containing compound **4** and the resulting solution was shaken for homogeneity. ^{1}H NMR ($CDCl_3$, 400 MHz, 25°C) δ = 8.61 (d, ^{3}J = 7.8Hz, 4H), 8.35 (s, 4H), 8.06 (ddd, J = 7.9, 7.8, 1.4Hz, 4H), 7.68 (d, ^{3}J = 5.1Hz, 4H), 7.50 (brm, 4H), 7.35 (dd, J = 6.2, 5.4Hz, 4H), 7.05-6.70 (brm, 20H), 5.26 (brs, 4H), 4.05 (brs, 8H), 3.79 (t, ^{3}J = 4.7Hz, 4H), 3.68-3.48 (m, 120H), 3.32 (s, 6H), 1.71 (tt, ^{3}J = 7.4, 6.9Hz, 4H), 1.43-1.36 (m, 4H), 1.31-1.15 (m, 16H), 0.83 (t, ^{3}J = 6.8Hz, 6H); ESI-MS: m/z calculated for $C_{152}H_{218}N_{10}O_{40}Zn$ $[M]^{2+}$ 1445.258; found 1445.394.

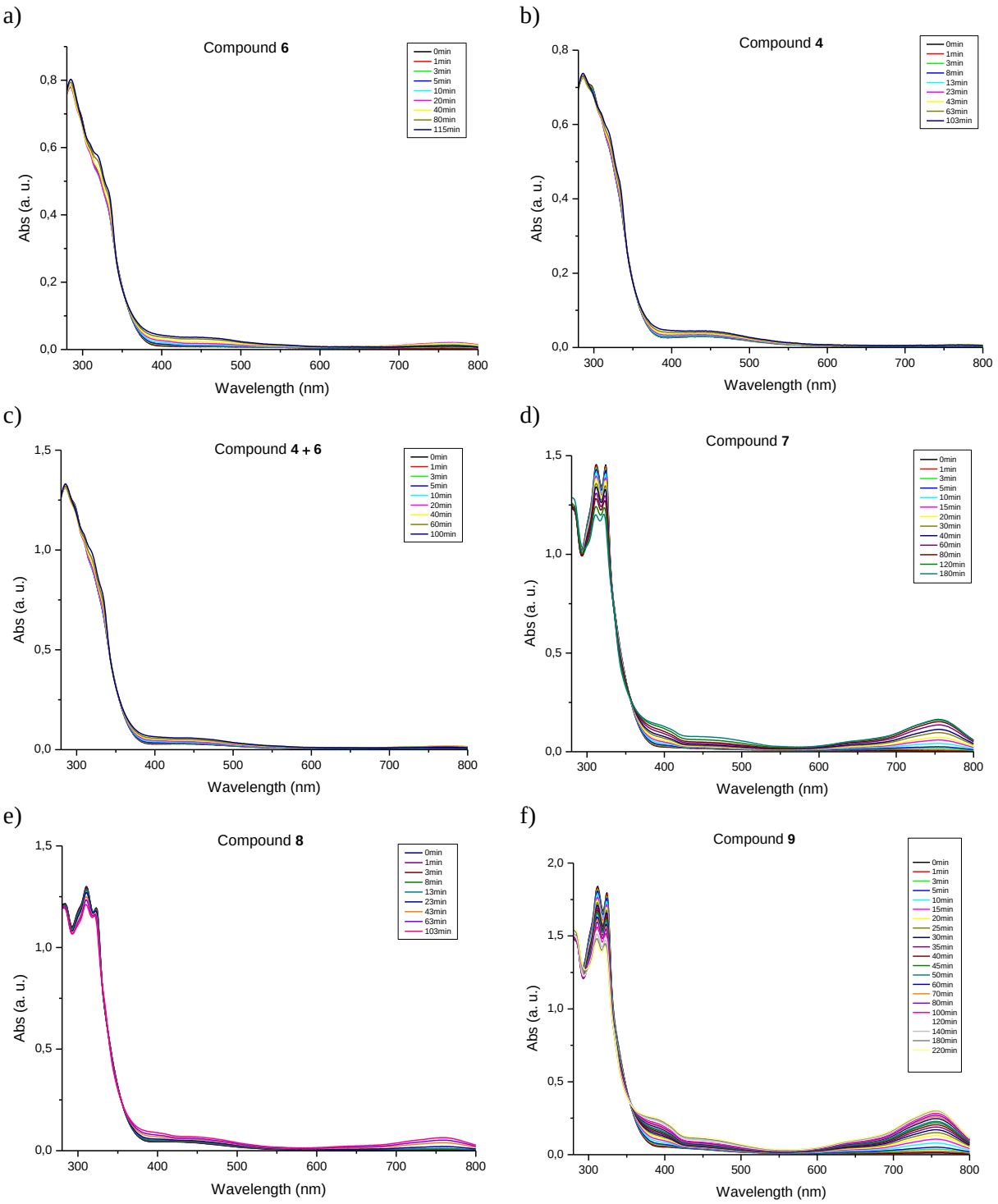
NMR Titration



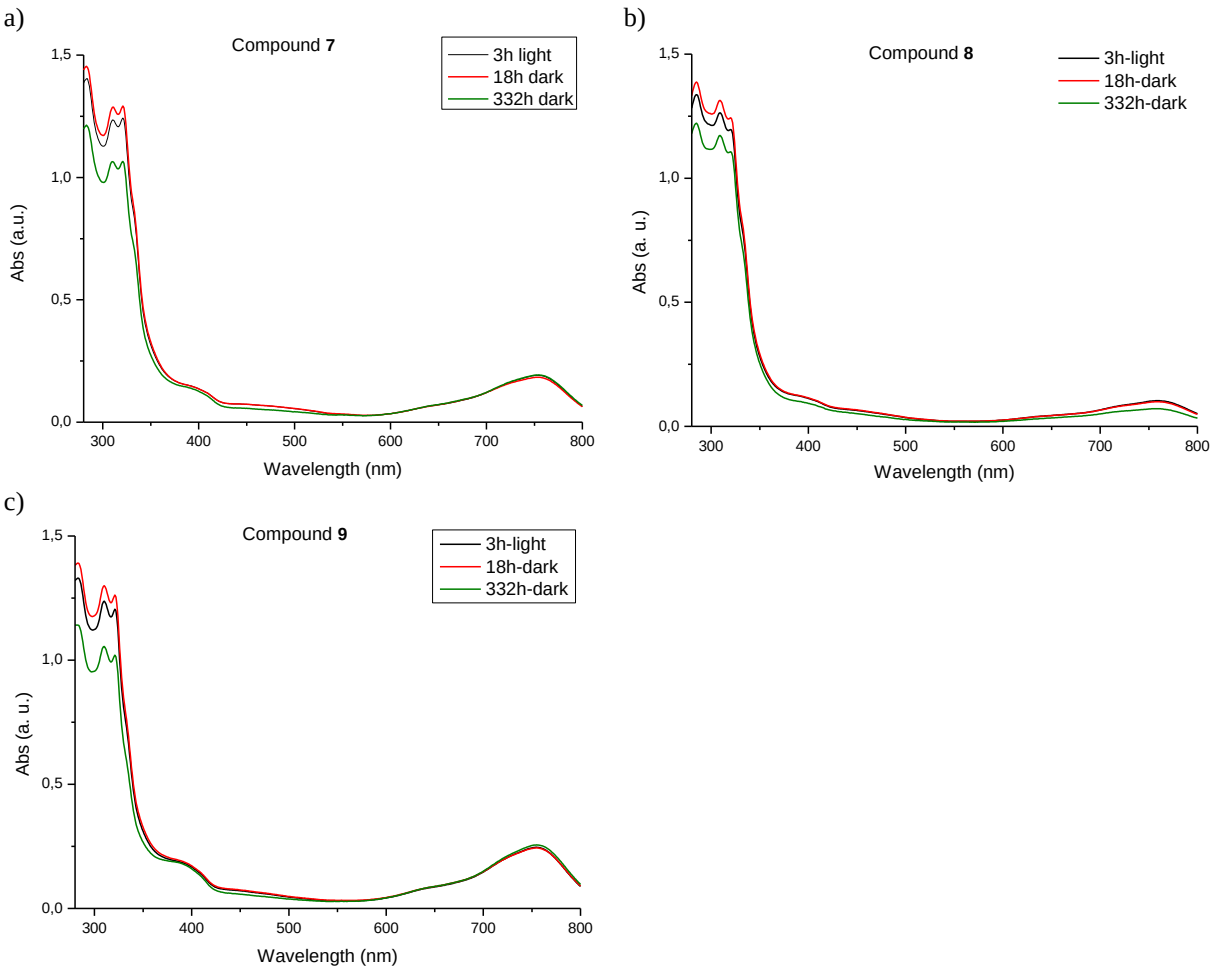
Supplementary Figure 1. ^{1}H NMR Titration of compound **6** (C = 10mM in $CDCl_3$) using $Zn(OTf)_2$ in CH_3OD to reach compound **7**.

UV-Vis Kinetic Measurements

Spectra were recorded using a UV-Vis-NIR spectrophotometer Cary 500 scan Varian.

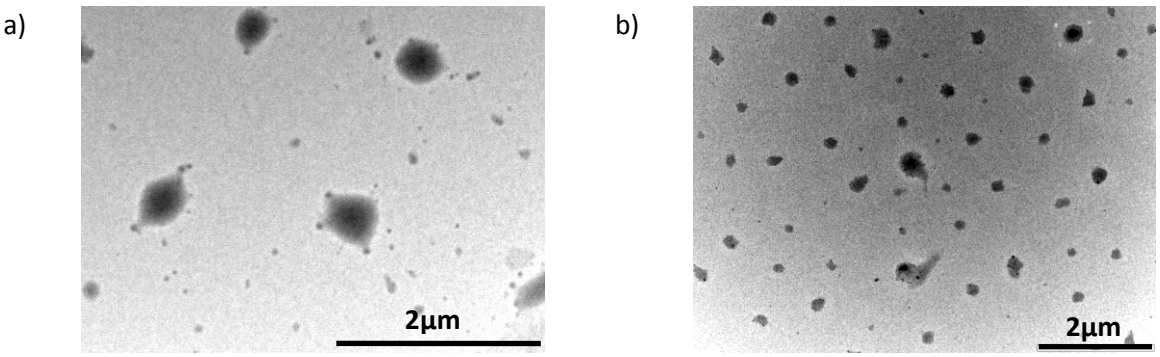


Supplementary Figure 2. UV-Vis-NIR spectra obtained as a function of time of irradiation for an initial 0.1 mM solution of compounds **4** (a), **6** (b), **4+6** (c), **7** (d), **8** (e), **9** (f) in chloroform.



Supplementary Figure 3. UV-Vis-NIR spectra obtained as a function of time of relaxation in the dark for an initial 0.1 mM solution of compounds **7** (a), **8** (b), **9** (c) in chloroform irradiated for 3h.

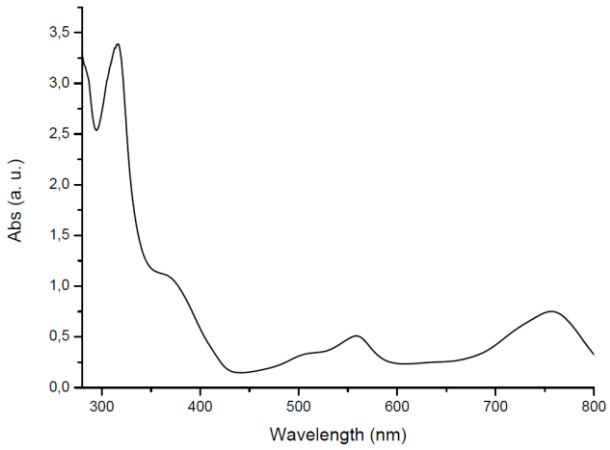
TEM Images



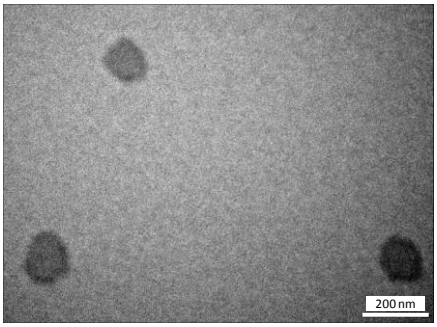
Supplementary Figure 4. Transmission electron micrographs of an irradiated solution of compounds **8** (a, [**8**] = 0.1mM in $CHCl_3$) and **9** (b, [**9**] = 0.1mM in $CHCl_3$).

Preparation and characterization of an iron complex from 6

A solution of iron chloride (1 mg, 2.8 µmol) in deuterated methanol (50 µL) was added to a solution of compound **6** (4.4 mg, 5.5 µmol) in deuterated chloroform (400 µL) and the resulting solution was shaken for homogeneity. After overnight irradiation, the solution was analyzed by ^{1}H NMR which led to broad signals as expected,[5] by UV-Vis-NIR (supplementary Figure 5) and TEM (supplementary Figure 6).



Supplementary Figure 5. UV-Vis-NIR spectra obtained for an initial 0.1 mM solution of complex Fe(II)$\mathbf{6}_2$ in chloroform after 4 hours of irradiation. The metal-to-ligand charge transfer band at 558 nm is characteristic for the Fe(II) complexes with terpyridine ligands,[5] while the 756 nm band is characteristic of the self-asembly.



Supplementary Figure 6. Transmission electron micrographs of an irradiated of complex Fe(II)$\mathbf{6}_2$ showing sizes and shapes similar to its Zn(II) analogue.

DLS Measurements

In the dynamic light scattering experiments (DLS), the normalised time autocorrelation function, $g^{(2)}(q,t)$, is measured as a function of the scattered wave-vector, q, given by $q=(4\pi n/\lambda)\sin(\theta/2)$, where n is the refractive index of the solvent (1.44 for $CDCl_3$ at 20 °C), and θ is the scattering angle. The measurements used a 3D DLS spectrometer (LS Instruments, Fribourg, Swiss) equipped with a 25mW HeNe laser (JDS uniphase) operating at λ=632.8 nm, a two channel multiple tau correlator (1088 channels in autocorrelation), a variable-angle detection system, and a temperature-controlled index matching vat (LS Instruments). The scattering spectrum was measured using two single mode fibre detections and two high sensitivity APD detectors (Perkin Elmer, model SPCM-AQR-13-FC).

Solutions were filtered before illumination through 0.2 μm Cellulose Millipore filter into the cylindrical scattering cell.

The experimental signal is the normalised time autocorrelation function of the scattered intensity:[6]

$$g^{(2)}(q,t) = \frac{\langle I(q,0)I(q,t)\rangle}{\langle I(q,0)\rangle^2} \quad \text{(SI-1)}$$

The latter can be expressed in terms of the field autocorrelation function or equivalently in terms of the autocorrelation function of the concentration fluctuations, $g^{(1)}(q,t)$, through:

$$g^{(2)}(q,t) - 1 = \alpha + \beta\left|g^{(1)}(q,t)\right|^2 \quad \text{(SI-2)}$$

Where α is the baseline (varying between 1×10^{-4} and 2×10^{-4} depending on the scattering angle and/or the system) and β the coherence factor, which in our experiments is varying between 0.7 and 0.9 depending on the samples. The normalised dynamical correlation function, $g^{(1)}(q,t)$, of polymer concentration fluctuations is defined as:

$$g^{(1)}(q,t) = \frac{\langle \delta c(q,0)\delta c(q,t)\rangle}{\langle \delta c(q,0)^2\rangle} \quad \text{(SI-3)}$$

Where δc(q,t) and δc(q,0) represent fluctuations of the polymer concentration at time t and zero, respectively.

In our experiments, solutions were characterised by a single relaxation mechanism with a characteristic relaxation time inversely proportional to q^2. The extrapolation of $(\tau_c q^2)^{-1}$ to q=0, where τ_c is the average relaxation time of $g^{(1)}(q,t)$, yields the mutual diffusion coefficient D. The latter is related to the average apparent hydrodynamic radius, R_H, of the species through the Stokes-Einstein relation:

$$D = \frac{k_B T}{6\pi\eta_s R_h} = \left(\frac{1}{\tau q^2}\right)_{q^2=0} \quad \text{(SI-4)}$$

Where k_B is the Boltzmann constant, η_s the solvent viscosity (0.57 cP for $CDCl_3$ at T=20°C), and T the absolute temperature.

For the determination of characteristic relaxation time τ we have adopted the classical Cumulant analysis[7] described as follows:

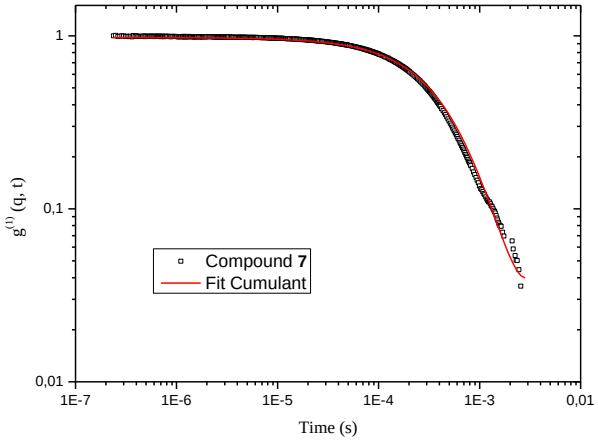
$$\ln g^{(1)}(t) \approx k_0 - k_1 t + \frac{k_2}{2}t^2 + \ldots \quad \text{(SI-5)}$$

Where $k_1 = 1/\langle\tau\rangle$ and k_2/k_1^2 is the polydispersity index (PDI).
We also used the Contin method[8] based on the inverse Laplace transform of $g^{(1)}(q,t)$. If the spectral profile of the scattered light can be described by a multi-Lorentzian curve, then $g^{(1)}(q,t)$ can be written as:

$$g^{(1)}(q,t) = \int_0^\infty G(\Gamma)\exp(-\Gamma t)d\Gamma \quad \text{(SI-6)}$$

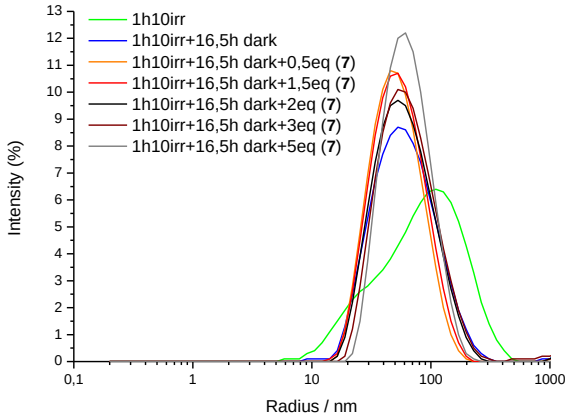
Where G(Γ) is the normalized decay constant distribution.

For example, supplementary figure 5 represents the normalised time autocorrelation function $g^{(1)}$ (q, t) for a solution of compound **7** and can be characterised by a simple exponential relaxation. Then the fit of $g^{(1)}$ (q, t) using Cumulant analysis gives an average hydrodynamic radius of 69 nm (the same value was obtained using Contin method).



Supplementary Figure 7. Time autocorrelation function of the scattered electric field vector for compound **7** ([**7**] = 0.1 mM in $CHCl_3$ at T=20°C and θ=90°). Solid red line: best fit using Cumulant analysis giving R_h=69 nm and polydispersity index PDI of 0.16.

Additional DLS experiments were performed using a ZetaSizer Nano ZS (Malvern Instruments, Worcestershire, U.K.). For this experiment, a 0.1mM solution of compound **7** was irradiated for 1h10 using a 20W power lamp. The solution was then left at rest in the dark for 16.5h and then, various quantities of compound **7** were added (50µL in total of a 11mM solution). The size of the objects was determined at each step and averaged over 5 measurements using the Stokes-Einstein relationship (see Supplementary Figure 8 and Supplementary Table 1).



Supplementary Figure 8. Distributions of hydrodynamic radii observed for compound **7** ([**7**] = 0.1 mM in $CHCl_3$ at T=25°C and θ=173°) just after irradiation, after 16.5h rest in the dark and following several additions of compound **7**.

[**7**]	0.1mM	0.155mM	0.265mM	0.32mM	0.43mM	0.65mM
Mean radius (nm)	70.7±4.2	55.7±3.0	58.5±1.6	67.0±1.9	71.5±3.1	68.0±1.8

Supplementary Table 1. Mean hydrodynamic radii observed for compound **7** after a 16.5h rest in the dark and when changing its concentration.

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