Electronic Supplementary Information

for

Luminescent supramolecular soft nanostructures in aqueous media from amphiphilic dinuclear Re(I) complexes

Cristina Cebrián,[a,+,†] Mirco Natali,[b,†] Davide Villa,[c,†] Monica Panigati,[c,*] Matteo Mauro,[a,d,*] Giuseppe D'Alfonso,[c] and Luisa De Cola[a,*]

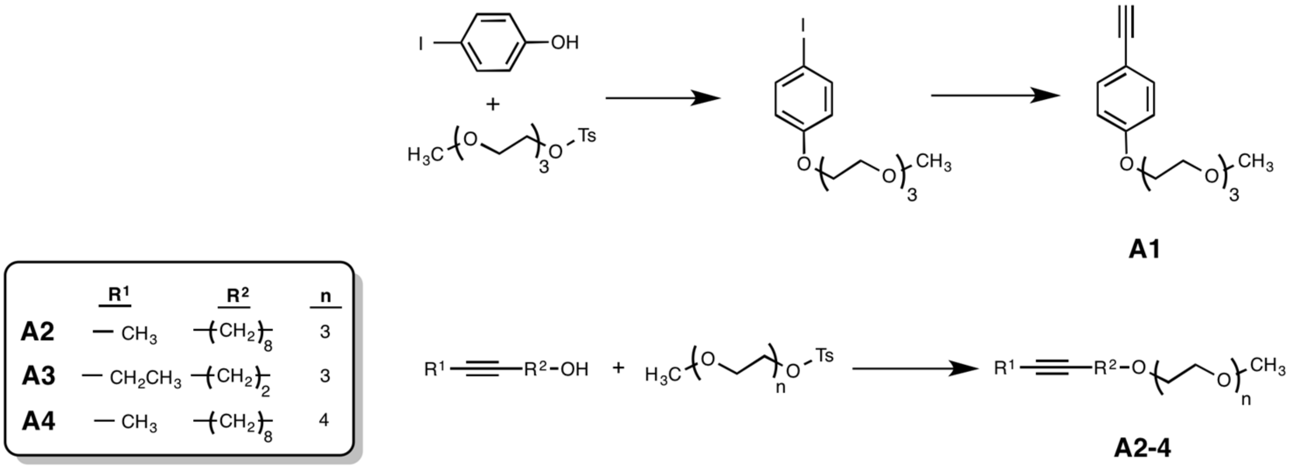
Experimental Section

General procedures. All the reactions were carried out under N_2 using the Schlenk technique. All the solvents were deoxygenated and dried by standard methods before use, while deuterated solvents were used as received. ^{1}H NMR spectra were recorded on a Bruker DRX400 spectrometer in CD_2Cl_2 solution at 300 K. High-resolution electrospray ionization mass spectrometry (HR-ESI-MS) was recorded on a MicroTOF (Bruker) mass spectrometer equipped with an electrospray source by the mass spectrometry service of the Institut de Chemie at the University of Strasbourg. IR spectra were acquired on a Bruker Vector 22 FT instrument in toluene solution. Elemental analyses were performed on a Perkin Elmer CHN2400 instrument. $[ReCl(CO)_5]$ was prepared according to literature method.[S. P. Schmidt, W. C Trogler, F. Basolo, *Inorg. Synth.* 1985, **23**, 41.] Tri- and tetraethylene glycol monomethyl ether (Aldrich), *p*-toluensulphonyl chloride (Fluka), 9-undecyn-1-ol (Aldrich), hex-3-yn-1-ol (Aldrich) and 4-iodophenol acetylene (Aldrich) were used as received.

Synthesis

Synthesis of the tri- and tetra-ethylene glycole tosylates. p-toluenesulfonyl chloride (22 mmol, 4.205 g) dissolved in 8 mL of CH_2Cl_2 was added dropwise, over one hour at 0°C, to a solution containing 20 mmol (9.71 g) of tetraethylene glycol monomethyl ether dissolved in 20 mL of CH_2Cl_2 and 30 mL of pyridine.

The mixture was stirred overnight at room temperature and the reaction was quenched by addition of concentrated HCl. The product was extracted with CH_2Cl_2 and the organic fractions were collected, dried with Na_2SO_4 and evaporated to dryness to leave a pale yellow oil, which was purified by column chromatography (silica gel, ethyl acetate : *n*-hexane, 9:1). The same procedure was followed for the synthesis of triethylene glycol tosylate. Solvents were evaporated to give 4.78 g (yield 60%) for (tetraethylene glycol) and 4.55 g (yield 65%) for (triethylene glycol) as a colourless oil in both cases. *Tetraethylene glycol tosylate*: ^{1}H NMR ($CDCl_3$) δ 7.81 (d, 2H, aromatic), 7.35 (d, 2H, aromatic), 4.17 (t, 2H, O_2SOCH_2), 3.72–3.53 (m, 14H, OCH_2), 3.36 (s, 3H, $-OCH_3$), 2.44 (s, 3H, $-CH_3$). *Triethylene glycol tosylate:* ^{1}H NMR ($CDCl_3$) δ: 7.80 (d, 2H, aromatic protons), 7.35 (d, 2H, aromatic protons), 4.16 (t, 2H, O_2SOCH_2), 3.69 (2H, t), 3.63–3.58 (6H, m), 3.54–3.52 (2H, m), 3.37 (3H, S, CH_3O), 2.45 (3H, s, CH_3Ph).



	R^1	R^2	n
A2	$-CH_3$	$-(CH_2)_8-$	3
A3	$-CH_2CH_3$	$-(CH_2)_2-$	3
A4	$-CH_3$	$-(CH_2)_8-$	4

Scheme S1. General schematic synthetic pathway followed for the preparation of the alkynes **A1**–**4**.

Synthesis of 1-iodo-4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzene. In a round-bottom flask 4-iodophenol (500 mg, 2.27 mmol), potassium carbonate (628 mg, 4.54 mmol) and tetrabutylammonium bromide (37 mg, 0.11 mmol) were sonicated for 15 minutes. Then, triethylene glycole tosylate (1.085 g, 3.41 mmol) is added to the reaction mixture and reacted over 15 hours at 90°C. 100 mL of ethyl ether were added and the crude is purified by silica plug using EtOH as the eluent. The solvent is evaporated under reduced pressure in order to obtain the desired intermediate as a dark brown liquid, namely 1-iodo-4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzene (0.75 g, yield 90%).

1-iodo-4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzene, ^{1}H NMR ($CDCl_3$, 298 K) δ: 7.54 (2H, d, H-2 and -6 Ph), 6.70 (2H, d, H-3 and -5 Ph), 4.10 (2H, t), 3.81 (2H, t), 3.71–3.68 (2H, m), 3.66–3.50 (6H, m), 3.34 (3H, s, CH_3).

Synthesis of 4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxyphenyl))ethynyltrimethylsilane. In a two-neck round-bottom flask 1-iodo-4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzene (4.0 g, 10.92 mmol) $Pd(PPh_3)_4$ (631 mg, 0.54 mmol) and copper iodide (35 mg, 0.18 mmol) were mixed in 50 mL $^i Pr_2NH$. The reaction mixture is purged with Ag for 30 minutes and ethynyltrimethylsilane is added (2.32 mL, 16.38 mmol) and the mixture heated at 80°C for 6 hours. Upon cooling, 40 mL of a saturated aqueous solution of NH_4Cl are added to the mixture and the aqueous phase is extracted with ethyl ether (3×30 mL) and the organic phase dried over anhydrous $MgSO_4$, filtered and the solvent evaporated to drieness. The desired product is isolated as brown liquid from the crude on silica gel column chromatography using *n*-hexane:AcOEt (4:1 → 2:1) as the eluent mixture (obtained 3.345 g, yield 91%).

4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxyphenyl))ethynyltrimethylsilane, ^{1}H NMR ($CDCl_3$, 298 K) δ: 7.39 (2H, d, H-2 and -6 Ph), 6.83 (2H, d, H-3 and -5 Ph), 4.10 (2H, t), 3.81 (2H, t), 3.71–3.68 (2H, m), 3.66–3.50 (6H, m), 3.34 (3H, s, CH_3), 0.24 (9H, s, $(CH_3)_3Si$).

Synthesis of 4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxyphenyl))acetylyne (**A1**). In a round-bottom flask 4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxyphenyl))ethynyltrimethylsilane (4.0 g, 11.88 mmol) are dissolved in a 1:1 mixture of MeOH:THF and K_2CO_3 (2.821 g, 17.83 mmol) is added. The resulting suspension is stirred for 30 minutes. The solvent mixture is removed under reduced pressure, the residue dissolved with 100 mL of chloroform, and washed with water (3×30 mL). The organic phase is dried over anhydrous $MgSO_4$ and evaporated under reduced pressure. The desired product **A1** is obtained as a brownish liquid (3.079 g, yield 98%).

4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxyphenyl))acetylyne (**A1**), ^{1}H NMR ($CDCl_3$, 298 K) δ: 7.41 (2H, d, H-2 and -6 Ph), 6.85 (2H, d, H-3 and -5 Ph), 4.13 (2H, t), 3.86 (2H, t), 3.74–3.64 (6H, m), 3.54–3.56 (2H, m), 3.38 (3H, s, CH_3), 2.99 (1H, s, CH).

Synthesis of the oligo-(ethylene oxide) alkynes (**A2–4**). The synthesis of the functionalized alkynes was carried out using the following general procedure. A sample of NaH (82.4 mg, 2.06 mmol, 60% paraffin dispersion) was washed with dry *n*-hexane (3×10 mL) under N_2. The solid residue was dispersed in freshly distilled THF (3 mL) and the suspension was cooled at 0°C. A sample of 9-undecyn-1-ol (200 µL, 1.03 mmol) was added dropwise and the reaction mixture was stirred at 0 °C for 3 hours. Then 1 equivalent of triethylene glycol tosylate (325 mg, 1.03 mmol, dissolved in a small amount of THF) was added. The temperature was slowly raised to room temperature and stirred overnight. The reaction was quenched by adding 10 mL of H_2O and the crude product was extracted with diethyl ether (3×10 mL). The organic fractions were collected, washed with 10 mL of brine and dried with anhydrous sodium sulfate. The resulting solution was evaporated to dryness, affording the crude product, which was purified by chromatography column (silica gel, ethyl acetate/*n*-hexane, 4:6). The fractions containing the product were collected and evaporated to dryness affording pure $CH_3C_2(CH_2)_8O(CH_2CH_2O)_3CH_3$ (**A2**) as colorless oil (0.60 mmol, isolated yield 58%). The same procedure was followed for $CH_3CH_2C_2(CH_2)_2O(CH_2CH_2O)_3CH_3$ (**A3**) and $CH_3C_2(CH_2)_8O(CH_2CH_2O)_4CH_3$ (**A4**).

Compound **A1**, ^{1}H NMR ($CDCl_3$, 298 K) δ: 7.41 (2H, d, aromatic protons), 6.85 (2H, d, aromatic protons), 4.13 (2H, t), 3.86 (2H, t), 3.74–3.64 (6H, m), 3.54–3.56 (2H, m) 3.38 (3H, s, CH_3), 2.99 (1H, s, C*H*).

Compound **A2**, ^{1}H NMR ($CDCl_3$, 298 K) δ: 1.27 (6H, m, aliphatic protons), 1.47 (4H, m, aliphatic protons), 1.59 (2H, m, aliphatic protons), 1.79 (3H, t, CH_3CC), 2.11 (2H, m, CCCH_2), 3.40 (3H, s, OCH_3), 3.44 (2H, t, OCH_2), 3.56 (4H, m, CH_2-CH_2O), 3.65 (8H, m, CH_2-CH_2O).

Compound **A3**, ^{1}H NMR ($CDCl_3$, 298 K) δ: 1.11 (3H, t, CH_2CH_3), 2.14 (2H, m, CH_2CC), 2.44 (2H, m, CCCH_2), 3.38 (3H, s, OCH_3), 3.57 (2H, m, CH_2-CH_2O), 3.67 (12H, m, CH_2-CH_2O).

Compound **A4**, ^{1}H NMR ($CDCl_3$, 298 K) δ: 1.27 (6H, m, aliphatic protons), 1.47 (4H, m, aliphatic protons), 1.59 (2H, m, aliphatic protons), 1.79 (3H, t, CH_3CC), 2.11 (2H, m, CCCH_2), 3.40 (3H, s, OCH_3), 3.44 (2H, t, OCH_2), 3.56 (4H, m, CH_2-CH_2O), 3.65 (12H, m, CH_2-CH_2O).

Synthesis of the 1,2-diazines: All the substituted pyridazines were prepared according to literature procedure involving, as first step, the synthesis of 1,2,4,5-tetrazine (from hydrazine hydrate and formamidine acetate) and then its reaction with the functionalized alkynes (see Scheme 1 of the main text). The functionalized pyridazines were used without further purification.

Synthesis of the complexes **1–4***:* The complexes (see Chart 1 for their structures and abbreviations) were prepared from $[ReCl(CO)_5]$, using the previously reported method. The crude products were purified by column chromatography (silica gel, ethyl acetate or petroleum ether/ethyl acetate, 1:1), affording pure yellow oily solids in high isolated yields (50–60%).

$[Re_2(\mu\text{-}Cl)_2(CO)_6$(μ-4-(4-(2-triethylene glycol monomethyl ethere)phenyl)pyridazine)] (**1**): ^{1}H NMR: (400 MHz, CD_2Cl_2) δ: 9.94 (d, *J* = 2.3 Hz, 1H), 9.65 (d, *J* = 6.3 Hz, 1H), 8.07 (dd, *J* = 6.2, 2.4 Hz, 1H), 7.84 (d, *J* = 8.8 Hz, 2H), 7.24 (d, *J* = 8.8 Hz, 2H), 4.30 (t, *J* = 4.6 Hz, 2H), 3.96–3.88 (m, 2H), 3.77–3.60 (m, 6H), 3.54 (dd, *J* = 5.7, 3.4 Hz, 2H), 3.37 (s, 3H). HR-ESI-MS for $[M+Na]^+$ calcd. 952.9634 found 952.9638. FT-IR (toluene) ν(CO) = 2049 (m), 2033 (s), 1945 (s), 1917 (s) cm^{-1}.

$[Re_2(\mu\text{-}Cl)_2(CO)_6$(μ-4-((8' tri-ethylene glycol-monomethyl-ether) octyl) -5-(methyl)pydz)] (**2**): ^{1}H NMR (400 MHz, CD_2Cl_2) δ 9.49 (s, 1H), 9.45 (s, 1H), 3.62–3.53 (m, 12H), 3.47 (t, *J* = 6.43 Hz, 2H), 3.38 (s, 3H), 2.86 (t, *J* = 7.9 Hz, 2H), 2.58 (s, 3H), 1.73 (q, *J* = 7.5 Hz, 2H), 1.60–1.40 (m, 10H). HR-ESI-MS for $[M+Na]^+$ calcd. 1003.0730 found 1003.0727. FT-IR (toluene) ν(CO) = 2048 (m), 2033 (s), 1944 (s), 1917 (s) cm^{-1}.

$[Re_2(\mu\text{-}Cl)_2(CO)_6$(μ-4-((3' tri-ethylene glycol monomethyl ether) propyl)-5-(ethyl)pydz)] (**3**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.63 (s, 1H), 9.45 (s, 1H), 7.28 (s, 6H), 3.89 (t, *J* = 5.6 Hz, 2H), 3.72–3.61 (m, 10H), 3.56 (dd, *J* = 5.9, 3.4 Hz, 2H), 3.39 (d, *J* = 0.6 Hz, 3H), 3.13 (t, *J* = 5.6 Hz, 2H), 2.94 (q, *J* = 7.6 Hz, 2H), 1.44 (t, *J* = 7.6 Hz, 3H). HR-ESI-MS for $[M+Na]^+$ calcd. 932.9947 found 932.9976. FT-IR (toluene) ν(CO) = 2049 (m), 2032 (s), 1946 (s), 1914 (s) cm^{-1}.

$[Re_2(\mu\text{-}Cl)_2(CO)_6$(μ-4-((8'tetra-ethylene glycol monomethyl ether) octyl)-5-(methyl)pydz)] (**4**): ^{1}H NMR (400 MHz, CD_2Cl_2) δ 9.44 (s, 1H), 9.41 (s, 1H), 3.66–3.58 (m, 16H), 3.47 (t, *J* = 6.43 Hz, 2H), 3.38 (s, 3H), 2.85 (t, *J* = 7.9 Hz, 2H), 2.60 (s, 3H), 1.73 (q, *J* = 7.5 Hz, 2H), 1.61–1.37 (m, 10H). HR-ESI-MS for $[M+Na]^+$ calcd 1047.1016 found 1047.0965. FT-IR (toluene) ν(CO) = 2049 (m), 2033 (s), 1946 (s), 1913 (s) cm^{-1}.

Photophysical characterization

Steady-state measurements. Absorption spectra were measured on a double-beam Shimadzu UV-3600 UV-Vis-NIR spectrophotometer and baseline corrected. Steady-state emission spectra were recorded on a HORIBA Jobin-Yvon IBH FL-322 Fluorolog 3 spectrometer equipped with a 450 W xenon arc lamp and a TBX-4-X single-photon-counting as excitation source and detector, respectively. Emission spectra were corrected for source intensity (lamp and grating) and emission spectral response (detector and grating) by standard correction curves. PLQY of samples in toluene were compared for **2–4** to *fac*-Ir(ppy)$_3$ (PLQY = 0.97 in degassed 2-MeTHF),[T. Sajoto, P. I. Djurovich, A. B. Tamayo, J. Oxgaard, W. A. Goddard III and M. E. Thompson, *J. Am. Chem. Soc.*, 2009, **131**, 9813.] while for **1** to Ru(bpy)$_3$Cl$_2$ (PLQY = 0.04 in air-equilibrated H_2O)[H. Ishida, S. Tobita, Y. Hasegawa, R. Katoh and K. Nozaki, *Coord. Chem. Rev.*, 2010, **254**, 2449.]. Photoluminescence quantum yields for samples in dioxane/water solvent mixtures were measured with a Hamamatsu Photonics absolute PL quantum yield measurement system (C9920-02) equipped with a L9799-01 CW Xenon light source (150 W), monochromator, C7473 photonic multi-channel analyzer, integrating sphere and employing U6039-05 PLQY measurement software (Hamamatsu Photonics, Ltd., Shizuoka, Japan).

Lifetime measurements. Lifetimes were measured with a FluoTime 300 "EasyTau" apparatus (PicoQuant) equipped with subnanosecond LDH sources (375, 405, 440, 510 and 640 nm, with 50–100 ps pulsewidth) powered by a PicoQuant PDL 820 variable (0.2–80 MHz) pulsed power supply. A PMA-C was employed for detection in the UV-visible (200–900 nm). Measurements were performed using a NanoHarp 250 MCS (Multi Channel scaler Card) histogram accumulating real-time processor. The decays were analyzed by means of PicoQuant FluoFit Global Fluorescence Decay Analysis Software (PicoQuant GmbH, Germany).

Morphological characterization

The mean particle size and the broadness of distribution were obtained by photon correlation spectroscopy (Dynamic Light Scattering, DLS) using the CONTIN algorithm. Each measurement consisted of 70 single experiments and the results were represented as intensity distributions. The measurements were performed utilizing a Beckman CoulterNano C system (Beckman Coulter, Krefeld, Germany). The light source was a laser diode (λ = 658 nm) with a power of 30 mW. Scattered light was detected using a PMT. The software used for control and analysis was Beckman DelsaNano 2.21 (Beckman Coulter, Krefeld, Germany). Scanning Electron Microscopy (SEM) and Scanning Transmission Electron Microscopy (STEM) images were acquired on a Zeiss XB 1540 EsB machine with a Zeiss-Gemini column. For frozen aqueous samples, 3μL of each sample were applied on a glow-discharged 300 mesh quantifoil R2/2 EM grid, and then were vitrified using an automated plunger equipped with a temperature and humidity controlled chamber (Vitrobot, FEI Company, The Netherlands). Images were recorded with a TEM Tecnai F20 G2 (FEI Company, The Netherlands) equipped with a field emission gun operating at 200 kV on a 2k × 2k CCD camera (Ultrascan 1000, Gatan Inc., Pleasanton).

Figures

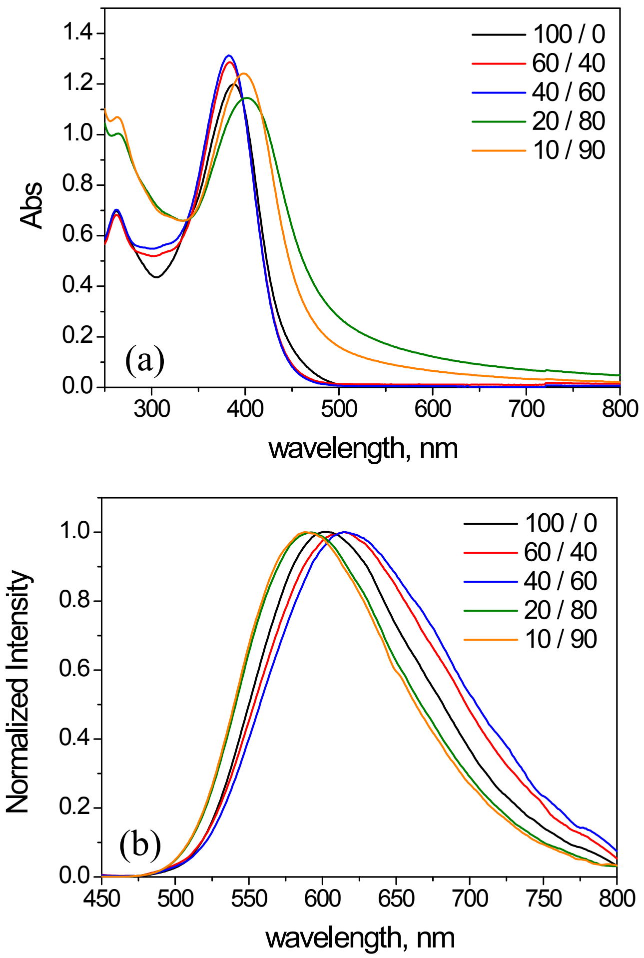


Figure S1. (a) Absorption spectra and (b) normalized emission spectra obtained for the metallo-surfactant **1** at concentration of 5.0×10^{-5} M in different dioxane/water ratio. Traces corresponding to 80/20 and 5/95 dioxane/water have been omitted for sake of clarity. For emission spectra, the samples were excited at $\lambda_{exc} = 430$ nm.

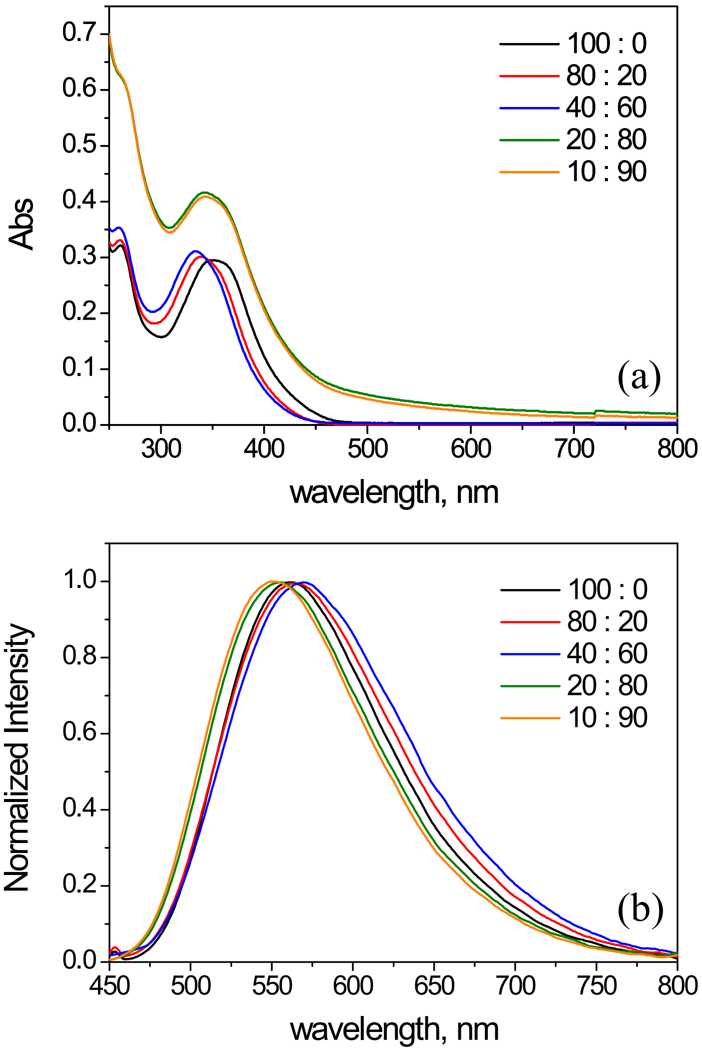


Figure S2. (a) Absorption spectra and (b) normalized emission spectra obtained for the metallo-surfactant **2** at concentration of 5.0×10^{-5} M in different dioxane/water ratio. Traces corresponding to 60/40 and 5/95 dioxane/water have been omitted for sake of clarity. For emission spectra, the samples were excited at λ_{exc} = 400 nm.

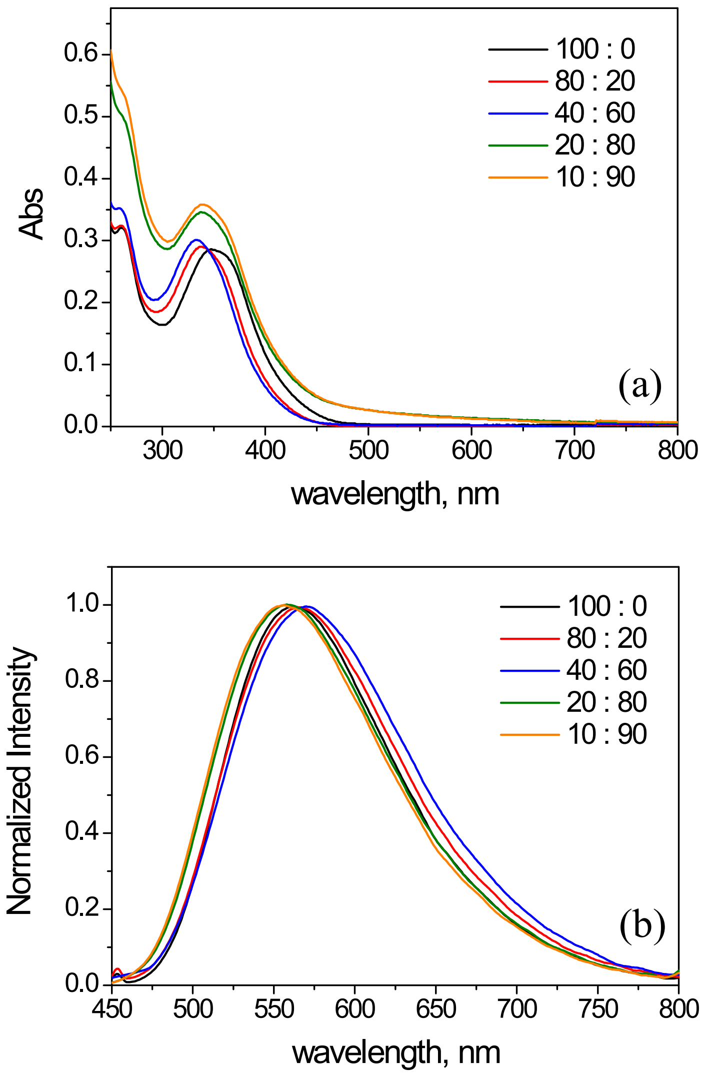


Figure S3. (a) Absorption spectra and (b) normalized emission spectra obtained for the metallo-surfactant **4** at concentration of 5.0×10^{-5} M in different dioxane/water ratio. Traces corresponding to 60/40 and 5/95 dioxane/water have been omitted for sake of clarity. For emission spectra, the samples were excited at λ_{exc} = 400 nm.

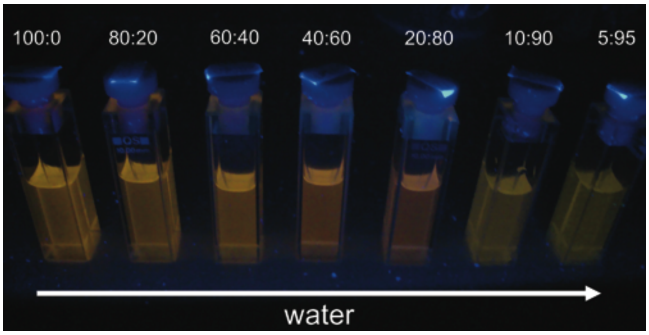


Figure S4. Picture of samples of **1** at concentration of 5.0×10^{-5} M in the different dioxane/water solutions upon irradiation with UV light, the change in emission intensity can be well discerned also by naked eye.

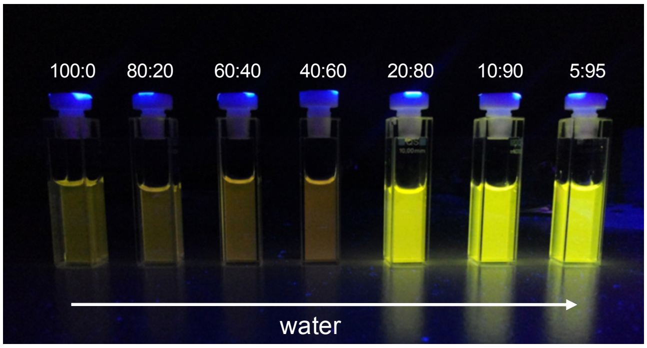


Figure S5. Picture of samples of **2** at concentration of 5.0×10^{-5} M in the different dioxane/water solutions upon irradiation with UV light, the change in emission intensity can be well discerned also by naked eye.

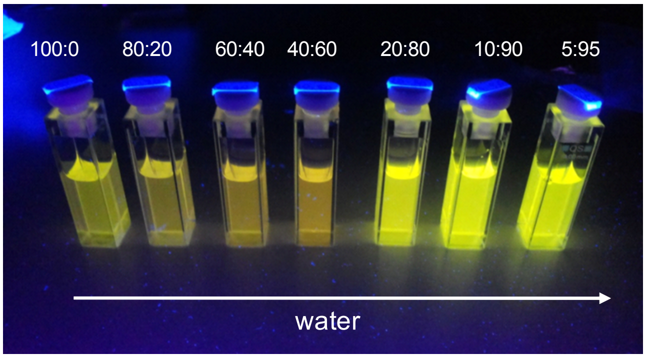


Figure S6. Picture of samples of **4** at concentration of 5.0×10^{-5} M in the different dioxane/water solutions upon irradiation with UV light, the change in emission intensity can be well discerned also by naked eye.

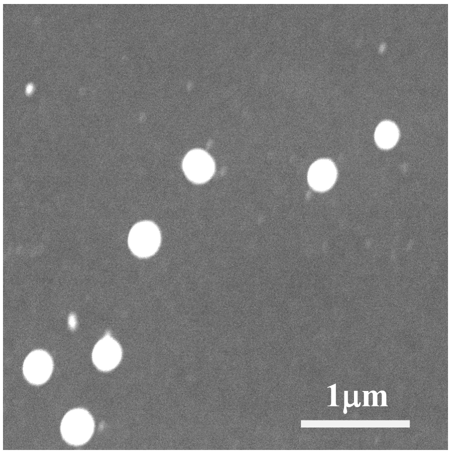


Figure S7. Dark-field STEM images obtained for samples of metallo-amphiphile **1** drop-casted onto a copper grid.

Table S1. Photophysical data for samples of the metallo-surfactant **2** at concentration of 5.0×10^{-5} M in air-equilibrated dioxane/water.

dioxane/water ratio	λ_{em}[a] [nm]	τ[b] [μs]	PLQY[c] (%)
100/0	560	0.39	0.02
80/20	564	0.40	0.03
60/40	567	0.41	0.03
40/60	570	0.51	0.03
20/80	555	0.55 (10%), 2.1 (90%)	0.13
10/90	550	0.9 (13%), 2.6 (87%)	0.15
5/95	548	1.0 (15%), 2.8 (85%)	0.17

[a] at room temperature, excitation wavelength at 400 nm; [b] at room temperature, excitation wavelength at 405 nm, analysis wavelength at 550 nm; [c] absolute quantum yields by means of an integrating sphere setup.

Table S2. Photophysical data for samples of the metallo-surfactant **4** at concentration of 5.0×10^{-5} M in air-equilibrated dioxane/water.

dioxane/water ratio	λ_{em}[a] [nm]	τ[b] [μs]	PLQY[c] (%)
100/0	562	0.40	0.02
80/20	566	0.39	0.02
60/40	568	0.39	0.03
40/60	570	0.54	0.03
20/80	558	0.51 (40%), 1.9 (60%)	0.07
10/90	555	0.60 (40%), 1.8 (60%)	0.08
5/95	555	0.6 (45%), 1.9 (55%)	0.08

[a] at room temperature, excitation wavelength at 400 nm; [b] at room temperature, excitation wavelength at 405 nm, analysis wavelength at 565 nm; [c] absolute quantum yields by means of an integrating sphere setup.

Table S3. DLS data obtained for metallo-amphiphile **1–4** at concentration of 5.0×10^{-5} M in different dioxane/water mixtures.

Entry[a]	dioxane/water	hydrodynamic diameter [nm]	polydispersity index (PDI)
1	40/60	–	–
1	20/80	337.7 ± 98.2	0.076
1	10/90	190.4 ± 61.5	0.061
1	5/95	–	–
2	40/60	–	–
2	20/80	318.5 ± 135.3	0.137[b]
2	10/90	224.5 ± 41.4	0.011
2	5/95	181.5 ± 27.3	0.087
3	20/80	–	–
3	10/90	463.7 ± 158.6	0.090
3	5/95	295.2 ± 105.5	0.098
4	40/60	–	–
4	20/80	170.6 ± 80.3	0.179[b]
4	10/90	221.7 ± 76.5	0.106[b]
4	5/95	135.6 ± 26.2	0.076

[a] 5.0×10^{-5} M solution; [b] PDI> 0.1 means not monodispersed distribution.