

Supporting information

Ultrasound-promoted hydrogelation of terpyridine derivatives

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Experimental Procedure

General Remarks. All the reactions were carried out under air atmosphere. Reagents were purchased from commercial sources and used as received.

NMR Spectroscopy. The NMR-spectra were recorded at 400 MHz for ¹H-NMR on a Varian Mercury 400 spectrometer, or at 600 MHz for ¹H- and at 150.8 MHz for ¹³C-NMR spectra on a Varian INOVA 600 spectrometer, in DMSO, CDCl₃ or CD₃CN as solvents. Coupling constants are in Hertz.

UV-Vis Spectroscopy. UV-Vis absorption spectra were measured on a Varian Cary 5000 double-beam 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, double grating excitation and emission monochromators (2.1 nm/mm dispersion; 1200 grooves/mm) and a Hamamatsu R928 photomultiplier tube or a TBX-4-X single-photon-counting detector. Emission and excitation spectra were corrected for source intensity (lamp and grating) and emission spectral response (detector and grating) by standard correction curves. Time-resolved measurements up to ~5 μs were performed using the time-correlated single-photon counting (TCSPC) option on the Fluorolog 3. NanoLEDs (295, 402, or 431 nm; FWHM < 750 ps)

with repetition rates between 10 kHz and 1 MHz were used to excite the sample. The excitation sources were mounted directly on the sample chamber at 90° to a double grating emission monochromator (2.1 nm/mm dispersion; 1200 grooves/mm) and collected by a TBX-4-X single-photon-counting detector. The photons collected at the detector are correlated by a time-to-amplitude converter (TAC) to the excitation pulse. Signals were collected using an IBH DataStation Hub photon counting module and data analysis was performed using the commercially available DAS6 software (HORIBA Jobin Yvon IBH). The goodness of fit was assessed by minimizing the reduced chi squared function (χ^2) and visual inspection of the weighted residuals.

SEM Characterization. The morphology of the gels was investigated using a Zeiss 1540 EsB dual beam focused ion beam/field emission scanning electron microscope with a working distance of 8mm. The samples were prepared by drop casting the gel samples on a silicon wafer and sputtering 4 nm of silver or gold after solvent evaporation. The imaging was performed at electronic high tension (EHT) values between 20 and 25 kV.

General Procedure for the Synthesis of terpyridine derivatives 1.

Compounds **1a**¹ and **1b**² were synthesized according to previously reported procedures.

Hydrochloride of 4'-(4-carboxyphenyl)-2,2':6',2''-terpyridine (1c): Compound **1b** (40 mg) was suspended in MeOH (5 ml) and an excess of HCl conc. (2 ml) was added. The mixture was stirred at room temperature for 24h and then the precipitate was filtered, washed with fresh MeOH and submitted to NMR analysis (>98% yields). ¹H NMR (400 MHz, D₆-DMSO): δ 7.65-7.70 (m, 2H), 8.10-8.25 (m, 6H), 8.80-8.85 (m, 6H). ¹³C NMR (150.8 MHz, D₆-DMSO): δ 121.5 (CH), 124.4 (CH), 127.3 (CH), 128.3 (CH), 130.8 (CH), 132.7 (C), 140.6 (C), 143.7 (CH), 146.3 (CH), 150.2 (C), 150.5 (C), 152.0 (C), 167.4 (C).

Hydrosulfate of 4'-(4-carboxyphenyl)-2,2':6',2''-terpyridine (1d): Compound **1b** (40 mg) was suspended in MeOH (5 ml) and an excess of H₂SO₄ conc. (1 ml) was added. The mixture was stirred at room temperature for 24h and then the precipitate was filtered, washed with fresh MeOH and submitted to NMR analysis (>98% yields). ¹H NMR (400 MHz, D₆-DMSO): δ 7.60-7.65 (m, 2H), 8.05-8.20 (m, 6H), 8.77 (d, 2H, *J*=7.6), 8.80-8.85 (m, 4H). ¹³C NMR (150.8 MHz, D₆-DMSO): δ 121.6 (CH), 124.6 (CH), 127.5 (CH), 128.3 (CH), 130.8 (CH), 132.8 (C), 140.5 (C), 144.0 (CH), 146.3 (CH), 150.2 (2C), 152.0 (C), 167.5 (C).

Sodium salt of 4'-(4-carboxyphenyl)-2,2':6',2''-terpyridine (1e): Compound **1b** (40 mg) was suspended in MeOH (5 ml) and NaOH (1 equiv.) was added. The mixture was stirred at room

¹ G. D. Storrier, S. B. Colbran *Inorg. Chim. Acta* **1999**, *284*, 76-84.

² E. C. Constable, E. L. Dunphy, C. E. Housecroft, M. Neuburger, S. Schaffner, F. Schaper, S.R. Batten *Dalton Trans.*, **2007**, 4323 – 4332.

temperature for 24h and then filtered, and the solvent evaporated. The obtained compound was washed with Et₂O and submitted to NMR analysis (>98% yields). ¹H NMR (400 MHz, D₆-DMSO): δ 7.50-7.55 (m, 2H), 7.75-7.85 (m, 2H), 8.00-8.10 (m, 4H), 8.65-8.70 (m, 2H), 8.73 (bs, 2H), 8.80-8.85 (m, 4H). ¹³C NMR (150.8 MHz, D₆-DMSO): δ 118.5 (CH), 121.6 (CH), 125.2 (CH), 126.3 (CH), 130.7 (CH), 137.7 (C), 138.1 (CH), 143.0 (C), 150.0 (CH), 150.3 (C), 155.7 (C), 156.3 (C), 169.2 (C).

Methyl 4-(2,2':6',2''-Terpyridin-4'-yl) benzoate (1f): Compound **1b** (40 mg) was suspended in MeOH (5 ml) and TMS-CH₂N₂ (1.0 M in THF) was added at 0°C until the yellow color persisted. The mixture was left to stir 4 h at room temperature, then the precipitate was filtered, washed with fresh MeOH and submitted to NMR analysis (>98% yields). ¹H NMR (400 MHz, CDCl₃): δ 3.97 (s, 3H), 7.37 (ddd, 2H, *J*= 1.2, *J*= 4.8, *J*= 7.5), 7.89 (dt, 2H, *J*= 1.8, *J*= 7.5), 7.95-8.00 (m, 2H), 8.15-8.20 (m, 2H), 8.68 (bd, 2H, *J*= 8.2), 8.74 (bd, 2H, *J*= 5.4), 8.76 (s, 2H). ¹³C NMR (150.8 MHz, D₆-CDCl₃): δ 52.4 (CH₃), 119.2 (CH), 121.6 (CH), 124.2 (CH), 127.6 (CH), 130.4 (CH), 130.7 (C), 137.1 (CH), 143.2 (2C), 149.4 (CH), 156.2 (C), 156.4 (C), 167.0 (C).

Hydrobromide of Methyl 4-(2,2':6',2''-Terpyridin-4'-yl) benzoate (1g): Compound **1f** (30 mg) was suspended in MeOH (5 ml) and an excess of HBr 48%. (2 ml) was added. The mixture was stirred at room temperature for 24 h and then the precipitate was filtered, washed with fresh MeOH and submitted to NMR analysis (>98% yields). ¹H NMR (400 MHz, D₆-DMSO): δ 3.90 (s, 3H), 7.60-7.70 (m, 2H), 8.05-8.20 (m, 6H), 8.75-8.85 (m, 6H). ¹³C NMR (150.8 MHz, D₆-CDCl₃): δ 53.2 (CH₃), 120.8 (CH), 123.7 (CH), 126.7 (CH), 128.4 (CH), 130.8 (CH), 131.4 (C), 141.5 (C), 142.0 (C), 147.7 (CH), 149.8 (CH), 152.2 (C), 153.6 (C), 166.4 (C).

General protocol for the synthesis of compounds 1h-l: The corresponding neutral forms of compounds **1h-l** were synthesized starting from the suitable aromatic aldehydes, according to a previously reported procedure.³ The obtained products (50 mg) were dissolved or suspended in MeOH (5 ml) and an excess of HBr 48%. (2 ml) was added. The mixtures were stirred at room temperature for 24 h and then the precipitates were filtered, washed with fresh MeOH. In all cases yields are almost quantitative.

Hydrobromide of 4'-(4-cyanophenyl)-2,2':6', 2''-terpyridine (1h): ¹H NMR (400 MHz, CD₃CN): δ 8.00-8.10 (m, 2H), 8.15-8.25 (m, 4H), 8.75-8.80 (m, 2H), 8.83 (s, 2H), 8.85-8.95 (m, 2H), 9.15-9.20 (m, 2H). ¹³C NMR (150.8 MHz, D₆-DMSO): δ 113.2 (C), 119.2 (CH), 121.7 (CH),

³ J. Wang, G. S. Hanan *Synlett* **2005**, 1251–1254

124.5 (CH), 127.4 (CH), 129.0 (CH), 134.0 (CH), 141.4 (C), 143.0 (CH), 146.8 (C), 149.5 (C), 150.9 (C), 152.9 (C).

Hydrobromide of 4'-(4-methoxyphenyl)-2,2':6', 2''-terpyridine (1i): ^1H NMR (400 MHz, D_6 -DMSO): δ 3.89 (s, 3H), 7.15-7.20 (m, 2H), 7.90 (bt, 2H, $J= 6.2$), 8.10-8.15 (m, 2H), 8.47 (bd, 2H, $J= 7.6$), 8.91 (s, 2H), 8.97 (bd, 2H, $J= 5.1$), 9.08 (d, 2H, $J= 7.6$). ^{13}C NMR (150.8 MHz, D_6 -DMSO): δ 56.2 (CH_3), 115.4 (CH), 121.0 (CH), 125.0 (CH), 127.7 (CH), 128.1 (C), 129.7 (CH), 145.0 (CH), 145.4 (CH), 149.3 (C), 150.5 (2C), 151.2 (C).

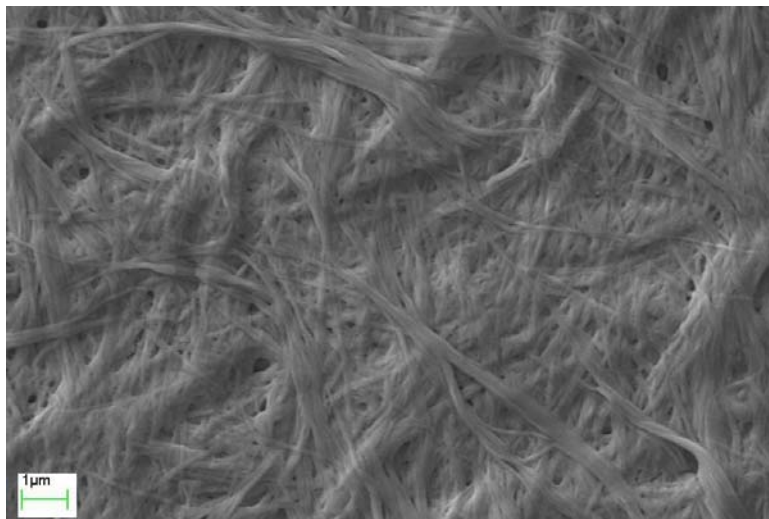
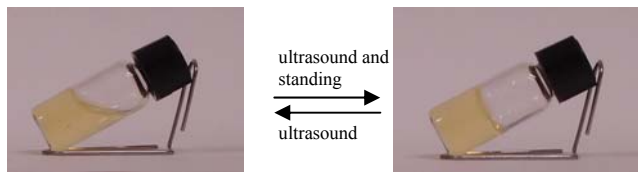
Hydrobromide of 4'-(2,4,6-trimethylphenyl)-2,2':6', 2''-terpyridine (1j): ^1H NMR (600 MHz, D_6 -DMSO): δ 2.02 (s, 6H), 2.31 (s, 3H), 7.03 (s, 2H), 7.70 (bt, 2H, $J= 6.8$), 8.26 (bt, 2H, $J= 8.0$), 8.32 (s, 2H), 8.80 (d, 2H, $J= 4.6$), 8.86 (d, 2H, $J= 8.0$). ^{13}C NMR (150.8 MHz, D_6 -DMSO): δ 21.0 (2 CH_3), 21.4 (CH_3), 124.8 (CH), 125.5 (CH), 127.7 (CH), 129.0 (CH), 135.4 (CH), 135.6 (C), 138.4 (C), 144.8 (C), 145.9 (CH), 149.9 (C), 151.0 (C), 153.6 (C).

Hydrobromide of 4'-(4-bromophenyl)-2,2':6', 2''-terpyridine (1k): ^1H NMR (400 MHz, D_6 -DMSO): δ 7.80-8.00 (m, 2H), 7.1 (d, 2H, $J= 7.5$), 8.00-8.15 (m, 2H), 8.35-8.55 (m, 2H), 8.75-9.20 (m, 6H). ^{13}C NMR (150.8 MHz, D_6 -DMSO): δ 122.0 (CH), 125.0 (CH), 125.3 (CH), 128.0 (C), 130.2 (CH), 133.0 (CH), 135.3 (C), 145.0 (CH), 145.5 (CH), 148.9 (C), 150.0 (2C).

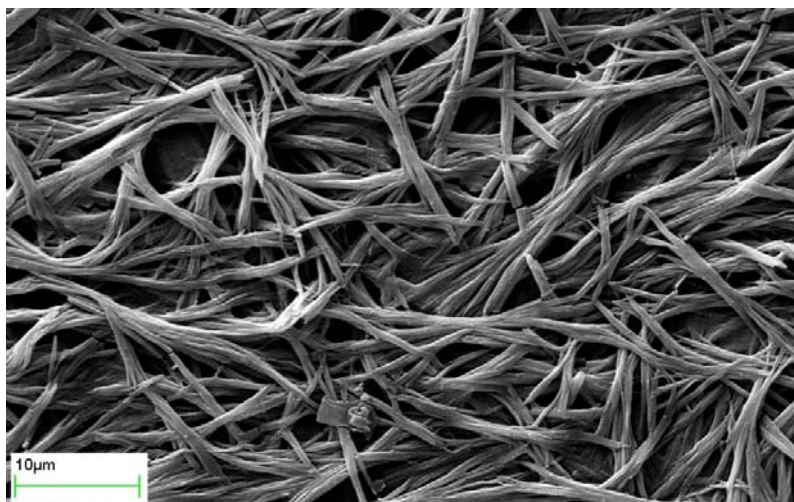
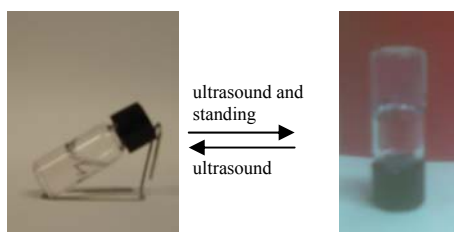
Hydrobromide of 4'-(4-hydroxyphenyl)-2,2':6', 2''-terpyridine (1l): ^1H NMR (400 MHz, D_6 -DMSO): δ 6.98 (d, 2H, $J= 8.5$), 7.65-7.80 (m, 2H), 7.90 (bd, 2H, $J= 8.5$), 8.28 (bt, 2H, $J= 7.2$), 8.77 (s, 2H), 8.80-8.95 (m, 4H). ^{13}C NMR (150.8 MHz, D_6 -DMSO): δ 116.8 (CH), 120.8 (CH), 125.1 (CH), 126.4 (C), 127.9 (CH), 129.7 (CH), 145.2 (CH), 145.4 (CH), 149.1 (C), 150.1 (C), 151.7 (C), 160.6 (C).

Gel tests and SEM images of the reported gels

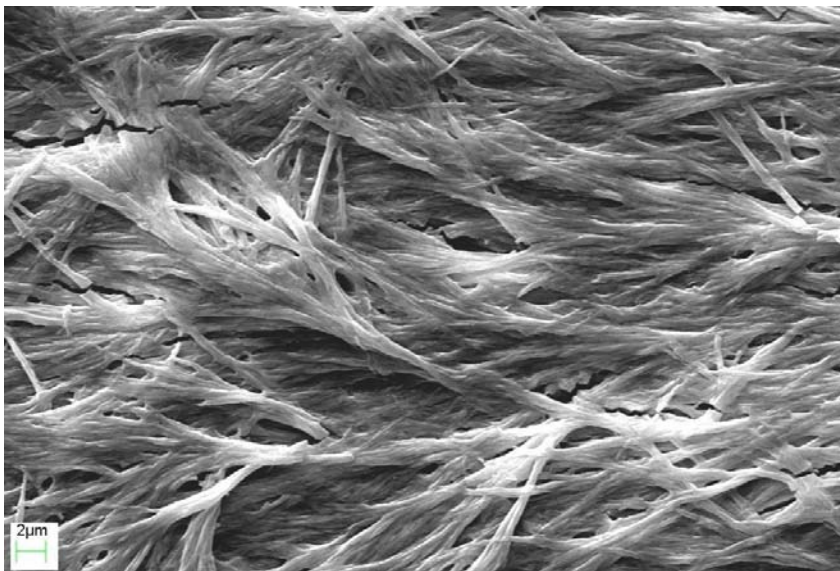
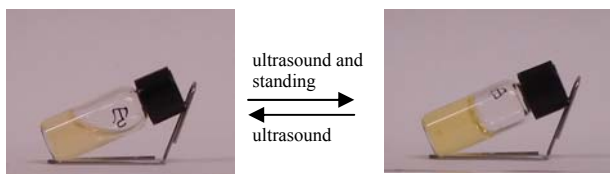
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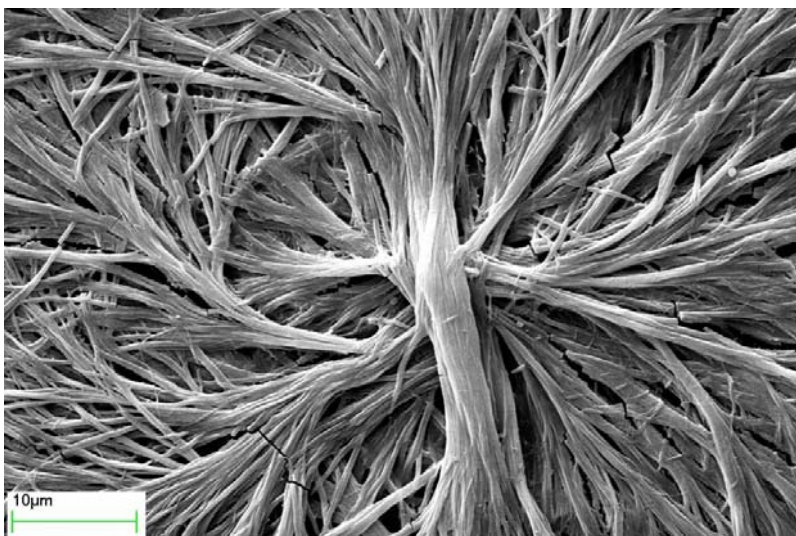
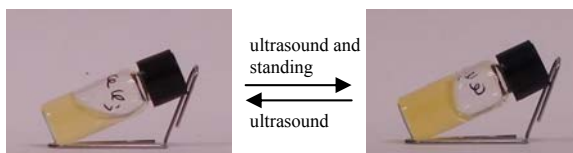
Hydrochloride of 4'-(4-carboxyphenyl)-2,2':6',2''-terpyridine (1c)



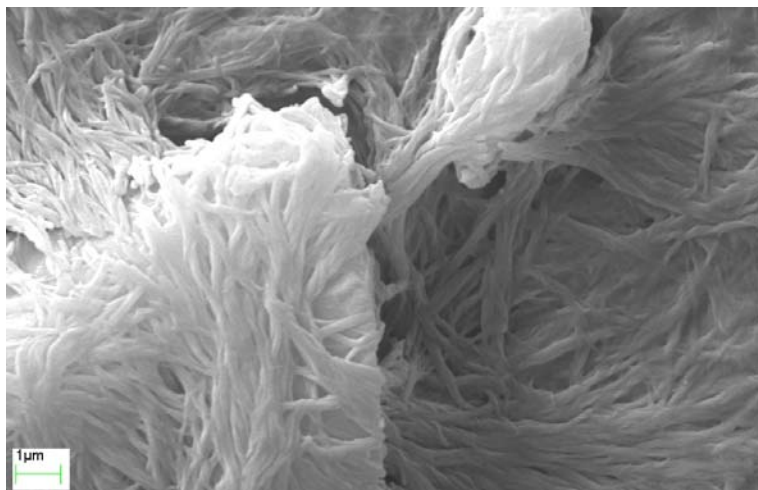
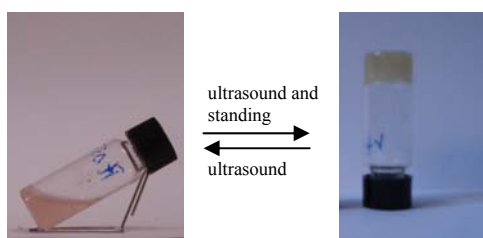
Hydrombromide of 4'-(4-carboxyphenyl)-2,2':6',2''-terpyridine (1a)-EuCl₃ 6H₂O



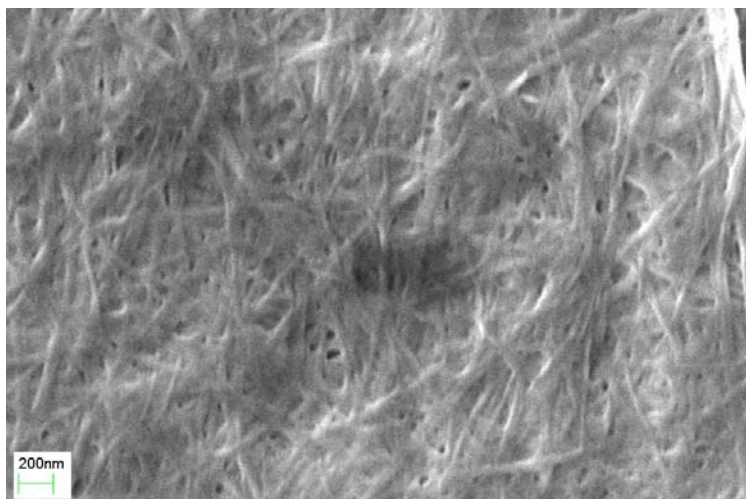
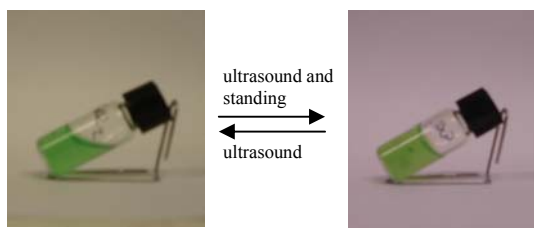
Hydrombromide of 4'-(4-carboxyphenyl)-2,2':6',2''-terpyridine (1a)-CeCl₃ 6H₂O



Hydrobromide of 4'-(4-carboxyphenyl)-2,2':6',2''-terpyridine (1a) -PtCl₂(PhCN)₂



Hydrobromide of 4'-(4-carboxyphenyl)-2,2':6',2''-terpyridine (1a) -CuCl₂ 6H₂O



UV-Vis absorption spectra of water diluted solutions (10^{-5} M ca) of the hydrogels

Besides the absorption spectra recorded on solid samples, we recorded also the absorbance of the solutions of the forming gels diluted in water to a concentration about 10^{-5} M.

The UV/Vis absorption spectra are very similar, showing a maximum around 276 nm. The recorded spectra of the metal-containing solutions resemble the absorption profiles of **1a** and **1c**. Only for **1a+CuCl₂**, a slight red-shift of the main peak is observed, together with the presence of a band broadening between 300 and 350nm.

