Self-assembly of nanocrystalline tetra-terpyridine complexes: from molecules to mesoscopic objects

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Materials and Methods

Unless otherwise stated, chemical reagents and solvents were purchased from Sigma-Aldrich. The experiments were carried out in air-equilibrated CH_2Cl_2 solution at 298 K. UV-Vis absorption spectra were recorded with a Perkin Elmer λ40 spectrophotometer using quartz cells with a pathlength of 1.0 cm. Fluorescence spectra were obtained with a Perkin Elmer LS-50 spectrofluorimeter. Global fitting of absorption and emission spectra has been performed by Specfit software. Dynamic light scattering (DLS) was used for determination of the size distributions employing a Malvern Nano ZS instrument with a 633 nm laser diode. Samples were housed in quartz cuvettes of 1 cm optical path length. The width of the DLS hydrodynamic diameter distribution is indicated by the PDI (polydispersion index). AFM imaging was performed using a Nanoscope Multimode 8 (Bruker, Santa Barbara, USA) equipped with a 15 μm piezoelectric scanner. The AFM was operated in tapping mode and in peak-force tapping mode. XRD analysis was carried out by means of a PANalytical X'Pert PRO diffractometer equipped with a Ni-filtered CuKα radiation and a fast X'Celerator detector.

Complexation study of TolTpy

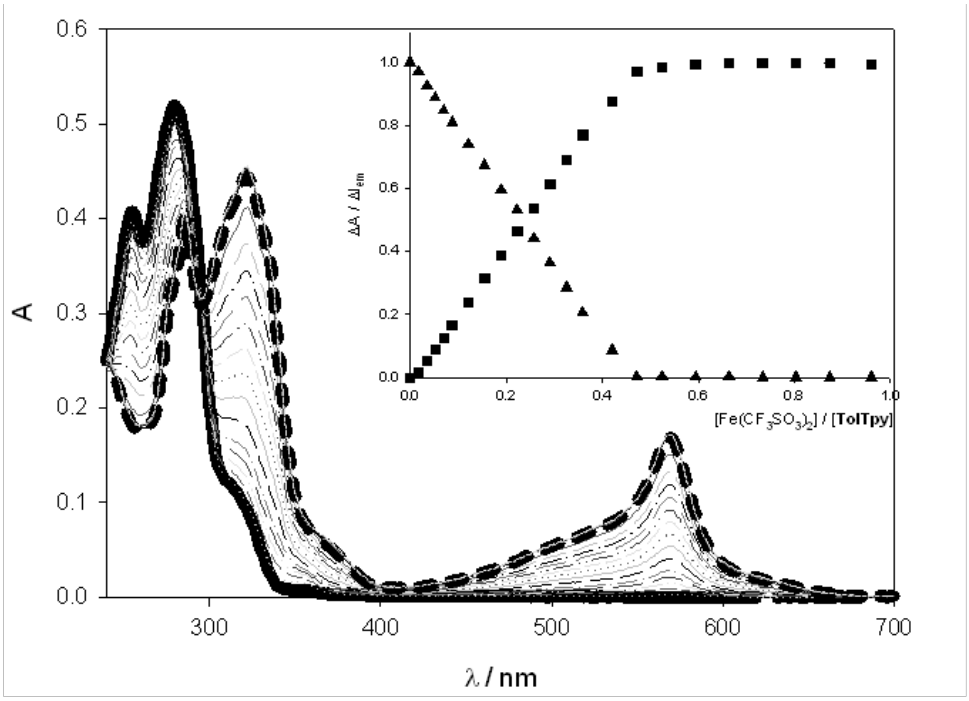

Figure SI-1. Absorption spectra of a 1.42 x 10^{-5} M solution of **TolTpy** in CH_2Cl_2 upon titration with $Fe(CF_3SO_3)_2$: 0 equiv (thick line), 0.6 equiv (dashed thick line). λ_{ex} = 305 nm (isosbestic point). Inset shows normalized emission intensity changes at 340 nm (triangles), and absorption changes at 575 nm (squares).

The absorption spectra show a red shift of the lowest energy band and the appearance of a band in the visible region due to a metal-to-ligand charge-transfer (MLCT) transition centered at 575 nm. Upon excitation at the isosbestic point, complete quenching of the fluorescence band at 340 nm was observed. The emission

quenching was expected on the basis of the fast non-radiative decay observed for the lowest energy MLCT excited state of the pristine $[Fe(tpy)_2]^{2+}$ complex. The plots of the absorption changes at 575 nm and the emission intensity at 340 nm are superimposed and reach a plateau at 0.5 equivalents of metal ion per **TolTpy**. These results demonstrate a 2:1 ligand to metal stoichiometry with an association constant logβ = 15, estimated by global fitting of the absorption spectra.

DLS supplementary data

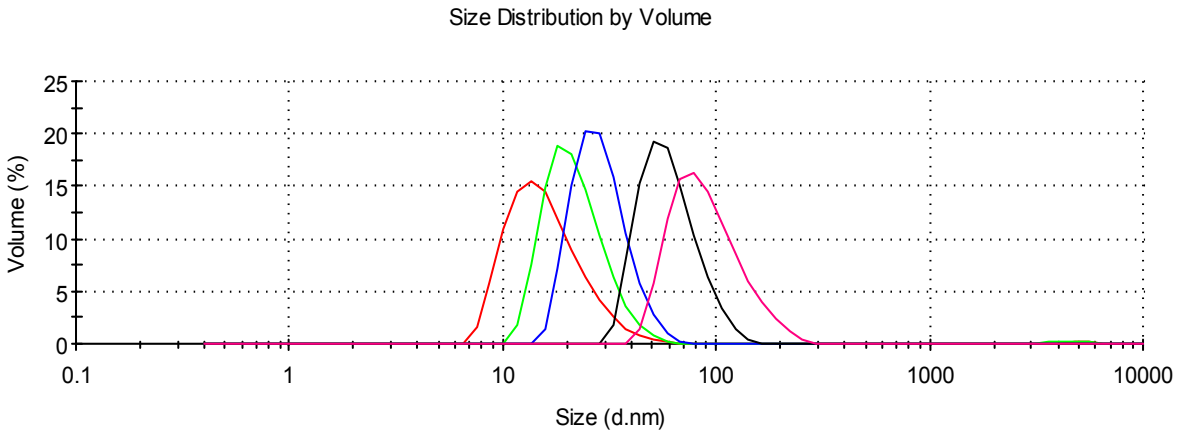

Figure SI-2. Dynamic Light Scattering plots of a 1.48 x 10^{-6} M solution of **TTT** in CH_2Cl_2 with 2 eqs. of $Fe(CF_3SO_3)_2$ after: five minutes (red), one hour (green), two hours (blue), four hours (black), six hours (pink).

In figure SI-2 are reported the data for **TTT** with 2 eqs. of $Fe(CF_3SO_3)_2$ over a period of six hours. Data were also collected for the ligand **TTT** however no significant scattering was observed confirming that the aggregates formed only with the addition of metal ions.

XRD data

TTT ***Main reflections, Peak List:***

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
5.5500	3605.46	0.2952	15.92379	7.70
6.6458	2367.10	0.2952	13.30053	5.05
7.7787	278.45	0.2952	11.36569	0.59
9.1485	31463.87	0.2952	9.66680	67.16
9.9673	46849.76	0.2952	8.87442	100.00
11.3572	9488.84	0.3444	7.79132	20.25
12.7336	11441.15	0.3444	6.95206	24.42
13.6328	5196.53	0.0900	6.49550	11.09

14.0653	6509.00	0.2952	6.29671	13.89
15.0553	13181.94	0.2952	5.88482	28.14
15.5508	10130.14	0.1968	5.69840	21.62
16.0624	17396.04	0.1997	5.51803	15.13
16.8366	10471.83	0.1968	5.26601	22.35
18.1998	22345.82	0.3444	4.87452	47.70
19.0941	29031.12	0.2952	4.64818	61.97
20.5001	22572.36	0.2952	4.33246	48.18
21.2935	17867.97	0.3444	4.17280	38.14
22.5387	17169.37	0.4920	3.94500	36.65
24.8687	18513.64	0.2952	3.58042	39.52
26.2010	6777.79	0.2460	3.40129	14.47
27.2222	5459.86	0.3444	3.27597	11.65
28.1994	2298.16	0.5904	3.16464	4.91
29.7267	2152.16	0.1968	3.00543	4.59

TTT.Fe ***Main reflections, Peak List:***

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
5.4153	5194.30	0.2460	16.31979	28.60
5.7167	8509.12	0.2210	15.45987	16.25
7.9750	684.40	0.1968	11.08642	3.77
9.1854	6714.48	0.3936	9.62801	36.97
9.7491	18162.62	0.2460	9.07256	100.00
10.8037	4352.73	0.3444	8.18923	23.97
11.3965	7881.71	0.2952	7.76457	43.40
14.7764	3172.84	0.1968	5.99524	17.47
15.0223	3310.60	0.1968	5.89764	18.23
16.2842	2998.71	0.1968	5.44336	16.51
18.3392	3898.56	0.0638	4.83780	21.46
18.8945	2650.17	0.2952	4.69685	14.59

20.5722	2484.73	0.2952	4.31743	13.68
23.8115	659.30	0.2952	3.73693	3.63
26.5971	542.04	0.1968	3.35154	2.98
27.9340	951.82	0.2952	3.19409	5.24
28.4854	941.29	0.3936	3.13351	5.18