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Supporting Information

Photoluminescent materials based on PMMA and a highly-emissive octahedral molybdenum metal cluster complex

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Experimental

Materials

$Cs_2[\{Mo_6I_8\}I_6]$ was synthesised according to earlier reported procedures.[1] Chemical reagents were purchased from Fisher, Aldrich or Alfa Aesar. Methyl methacrylate (MMA) was washed with an aqueous solution of NaOH (1 M) and dried first over magnesium sulfate and then stored over activated molecular sieves (3 Å) for at least 48 h prior to polymerisation. AIBN was recrystallised from methanol

Instrumentation

NMR spectra were recorded on a Bruker Avance 300 NMR spectrometer equipped with a solution-state dual channel probe working at 300.13 MHz for ^1H and 75 MHz for ^{13}C. NMR spectra were measured in $CDCl_3$ ($\delta_H = 7.26$, $\delta_C = 77.16$ ppm) in the standard way using the zg30 pulse program for ^1H and waltz16 pendant pulse program for ^{13}C. FTIR was recorded on a Bruker Vertex 80 as KBr discs. Absorption spectra were recorded in diapason 270-700 nm on a PerkinElmer Lambda35 UV/Vis spectrometer. Thermal transition temperatures were determined under an N_2 atmosphere using a Mettler Toledo DSC 1 differential scanning calorimeter. The heating and cooling rates were kept at 20 °C/min, with sample weights approximately 3.0-5.0 mg. Indium was utilised as a reference for calibrating the temperature. T_g was estimated as the midpoint temperature of the endothermic baseline shift. Polymer decomposition temperatures (T_d) were found by thermogravimetric analysis (TGA) of polymer samples (~3 mg) on a PerkinElmer Pyris 1 in a stream of nitrogen (30 $mL\cdot min^{-1}$) at a heating rate of 10 $K\cdot min^{-1}$ and reported as temperatures of onset of intense thermal degradation determined by the point of intersection of the tangents to two branches of the thermogravimetric curves. Polymer molecular masses (M_n) were determined using gel permeation chromatography (GPC) using a degassed THF eluent system containing 2% TEA and 0.05% (w/v) BHT through three PL gel 5 µm 300 x 7.5 mm mixed C columns. The system, operating at 40 °C with an eluent flow rate of 1 mL·min^{-1}, was calibrated against narrow polystyrene standards (M_p ranged from 162 to 6 035 000 g·mol^{-1}).

Synthesis

[2-(Methacryloyloxy)ethyl]dimethyldodecylammonium iodide (*dMDAEMA*I). A mixture of 2,2-dimethylaminoethyl methacrylate (5 mL, 0.030 mol) and 1-iodododecane (7.5 mL, 0.030 mol) were dissolved in chloroform (50 mL) and heated at 50 °C for 18 h. The reaction mixture was concentrated using a rotary evaporator and precipitated in cold diethyl ether. The obtained white solid was collected by filtration and dried under vacuum. Yield: 12.0 g (88%). Elemental analysis (%): Found C 53.1, H 9.0, N 3.2; Calculated for $C_{20}H_{40}INO_2$: C 53.0, H 8.9, N 3.1. NMR ($CDCl_3$) – $\delta(^1H)$: 6.15 [1H, s, $C\mathit{H}H$], 5.68 [1H, s, $CH\mathit{H}$], 4.65 [2H, m, $OC\mathit{H}_2$], 4.13 [2H, m, $C\mathit{H}_2N$]. 3.62-3.58 [2H, m, $NC\mathit{H}_2$] 3.49 [6H, s, $N(C\mathit{H}_3)_2$], 1.94 [3H, s, $C\mathit{H}_3$], 1.75 [2H, m, $CH_2C\mathit{H}_2$], 1.40-1.12 [18H, $(C\mathit{H}_2)_9$], 0.86 [3H, t, J = 6.7 Hz, $C\mathit{H}_3$]. $\delta(^{13}C)$: 166.3, 135.1, 127.5, 65.8, 62.5, 58.1, 31.9, 29.6-28.5, 26.2, 23.0, 22.7. FTIR (cm^{-1}): 2918, 2850, [δ(CH)], 1721 [δ(C=O)], 1632 [δ(C=C)], 1464 [$\upsilon_s(CH_3)$], 1298 [υ_{as}(C–O–C)], 1167 [υ_s(C–O–C)], 961 [$\delta(-(CH_2)_n]$.

(*dMDAEMA*)$_2$[{Mo$_6$I$_8$}I$_6$] (1). 1.0 g (0.38 mmol) of $Cs_2[\{Mo_6I_8\}I_6]$ and 1.0 g (2.21 mmol) of *dMDAEMA*I were stirred in acetone (150 mL) for 24 h. The obtained solution was filtered and the solvent was evaporated. The solid residue was washed with a 1:1 mixture of CH_3OH/H_2O giving a maroon-coloured powdered product. Yield: 0.82 g (72%). Elemental analysis (%): Found C 16.3, H 2.5, N 1.0; Calculated for $C_{40}H_{80}I_{14}Mo_6N_2O_4$: C 16.0, H 2.7, N 0.9. NMR ($CDCl_3$) – $\delta(^1H)$: 6.17 [1H, s, $C\mathit{H}H$], 5.74 [1H, s, $CH\mathit{H}$], 4.71 [2H, m, $OC\mathit{H}_2$], 3.93 [2H, m, $C\mathit{H}_2N$]. 3.40 [8H, m, $NC\mathit{H}_2$+$N(C\mathit{H}_3)_2$], 1.97 [3H, s, $C\mathit{H}_3$], 1.67 [2H, m, $NC\mathit{H}_2$], 1.40-1.12 [18H, $(C\mathit{H}_2)_9$], 0.87 [3H, t, J = 6.7 Hz, $C\mathit{H}_3$]. FTIR (cm^{-1}): 2918, 2849, [δ(CH)], 1715 [δ(C=O)], 1635 [δ(C=C)], 1455 [$\upsilon_s(CH_3)$], 1384, 1291 [υ_{as}(C–O–C)], 1152 [υ_s(C–O–C)], 941 [$\delta(-(CH_2)_n]$.

(*dMDAEMA*)$_2$[{Mo$_6$I$_8$}(OTs)$_6$] (2). 500 mg (0.166 mmol) of **1** and 325 mg (1.16 mmol) of AgOTs were added to 100 mL of dry dichloromethane in a Schlenk tube. The mixture was stirred for 7 days in a flask covered by alumina foil at room temperature. After this time, the mixture had become amber in colour and, upon exposure to UV light, gave an intense red coloured emission. The solution was filtered and concentrated under vacuum. Layering of diethyl ether on top of a dichloromethane solution precipitated the product as a fine orange powder. The product was isolated by centrifugation (4000 rpm, 2 min), washed twice with diethyl ether (30 mL), dried under vacuum and stored in a vacuum desiccator. Yield: 278 mg (51%). Elemental analysis (%): Found C 30.4, H 4.2, N 1.0, S 5.5; Calculated for $C_{82}H_{122}I_8Mo_6N_2O_{22}S_6$: C 30.1, H 3.8, N 0.9, S 5.9. NMR ($CDCl_3$) – $\delta(^1H)$: 7.51 [12H, d, J = 8.2 Hz, 6*2*H^{ortho}], 7.12 [2H, d, J = 8.2 Hz, 6*2*H^{meta}] 6.04 [2H, s, 2*$C\mathit{H}H$], 5.57 [1H, s, 2*$CH\mathit{H}$], 4.52 [4H, m, 2*$OC\mathit{H}_2$], 3.76 [4H, m, 2*$C\mathit{H}_2N$]. 3.27 [12H+4H, s, 2*($N(C\mathit{H}_3)_2$+$NC\mathit{H}_2$)], 2.31 [18H, s, 6*$C\mathit{H}_3$] 1.84 [6H, s, 2*$C\mathit{H}_3$], 1.50 [4H, m, 2* $CH_2C\mathit{H}_2$], 1.32-1.08 [36H, 2*$(C\mathit{H}_2)_9$], 0.81 [6H, t, J=6.7 Hz, 2*$C\mathit{H}_3$]; $\delta(^{13}C)$: 166.3, 135.1, 127.5, 65.5, 62.4, 58.0, 31.9, 29.7-29.1, 26.3, 22.8, 22.7 (*dMDAEMA*$^+$), 141.3, 139.6, 129.2, 126.4, 21.5 (OTs$^-$). ESI-MS$^+$: Found for *dMDAEMA*$^+$ 326.26, Calc. 326.53. ESI-MS$^-$: Found for $[\{Mo_6I_8\}(OTs)_6]^{2-}$ 1308.81, Calc. 1309.02. FTIR: 2951, 2923, 2852 [δ(CH)], 1720 [δ(C=O)], 1635 [δ(C=C)], 1458 [$\upsilon_s(CH_3)$], 1272, 1197, ($\upsilon_a(SO_2)$), 1157 [$\upsilon_s(SO_2)$], 980 υ(SO), 567 [δ(CS)].

General procedure for bulk polymerisation. Samples denoted as PMMA$_{bulk}$-Mo^x (where *bulk* refers to the fact that no solvent was used during the polymerisation process and *x* refers to the content of **2** in mg per 1 mL of monomer) were synthesised using the following protocol. Solutions of **2** in MMA in concentrations 0.10, 0.25, 1.0, 2.0 and 4.0 mg/mL were prepared, using an ultrasound bath to assist sample dissolution, and degassed by purging with nitrogen. Sample tubes were filled with 1 mL of the solutions and AIBN (10 mg, 0.6 wt%). Each tube was sealed with a rubber septum, cooled down to –77 ºC and degassed by three short (~ 1 min) vacuum/nitrogen cycles. The mixture was then kept for 18 h at 70 °C to yield polymer pellets. A pellet of neat $\text{PMMA}_{\text{bulk}}$ was also prepared as a control following the same procedure.

General procedure for solution polymerisation. Samples denoted as $\text{PMMA}_{\text{solut}}\text{-Mo}^{x}$ (where *solut* refers to the fact that a solvent was used for dissolution during the polymerisation and *x* refers to the content of 2 in mg per 1 mL of monomer) were synthesised by the following protocol: **2** (5, 10, 50, or 100 mg) was dissolved in 5 mL of freshly degassed extra dry chlorobenzene using an ultrasound bath and gentle heating to assist sample dissolution. Freshly degassed MMA (1 mL), AIBN (10 mg, 0.6 wt%) and a magnetic follower were added to each solution. Each mixture was sealed with a rubber septum, sonicated for 5 minutes, degassed by purging with nitrogen for 10 minutes and heated at 70 ^{o}C for 18 h. The resultant solutions were each mixed with 10 mL of toluene and precipitated in hexane (150 mL). The powdered precipitate of each polymer was collected by filtration and dried under vacuum. A sample of neat PMMA (as a control) was also prepared following the same procedure.

Photoluminescence Measurements

For photoluminescence measurements, powdered samples of compound **2** and of cluster-containing copolymers were placed between two non-fluorescent glass plates. The absorbance of an acetonitrile solution of **2** was set at < 0.1 at 355 nm. The solution of **2** was poured into a quartz cuvette and deaerated, by purging an Ar-gas stream through the solution for 30 min, and then the cuvette was sealed. Measurements were carried out at 298 K. The samples were excited by 355-nm laser pulses (6 ns duration, LOTIS TII, LS-2137/3). Corrected emission spectra were recorded on a red-light-sensitive multichannel photodetector (Hamamatsu Photonics, PMA-11). For emission decay measurements, the emission was analysed by a streak-scope system (Hamamatsu Photonics, C4334 and C5094). Lifetimes were determined using the software U8167-01, Version 1.3.0 from Hamamatsu Photonics; the quality of fit was judged by the chi-squared values obtained by the fitting program. The emission quantum yields were determined by an Absolute Photo-Luminescence Quantum Yield Measurement System (Hamamatsu Photonics, C9920-03), comprised of an excitation xenon light source (the excitation wavelength was set at 400 nm), an integrating sphere, and a red-sensitive multichannel photodetector (Hamamatsu Photonics, PMA-12).

Fabrication and Characterisation of Electrospun Fibres

To obtain polymer fibres, solutions of the powdered polymers $\text{PMMA}_{\text{solut}}\text{-Mo}^{x}$ (where x = 5.0, 10, 50, or 100) in chloroform (25 wt%) were electrospun from needle with 1.2 mm inner diameter under the following constant conditions: a flow rate of 2 mL/h, a working distance of 9 cm, and an applied positive voltage of 12 kV. The electrospinning apparatus was equipped with a high voltage power supply (Genvolt, 0–30 kV voltage power source), digitally controlled syringe pump (model no. Alladin-8000, World Precision Instruments, UK) and an aluminium/plastic gripping flat plate grounded collector. The electrospinning device was enclosed in a perspex box and the electrospinning process was performed at ambient temperature and at 45–50% relative humidity. The electrospun fibres were collected on either a glass slide or on aluminium foil. The size and morphology of the fibres were characterised by scanning electron microscopy (SEM) using a JEOL JSM-5700 CarryScope microscope. The unity of emission from fibers was characterised using a Zeiss LSM 780 NLO (Carl Zeiss Inc., Jena, Germany) on an AxioObserver Z1 (Zeiss) equipped with a laser diode (405 nm) for fluorescence and with a APOCHROMAT 63x/1.4 Oil DIC LD Plan objective.

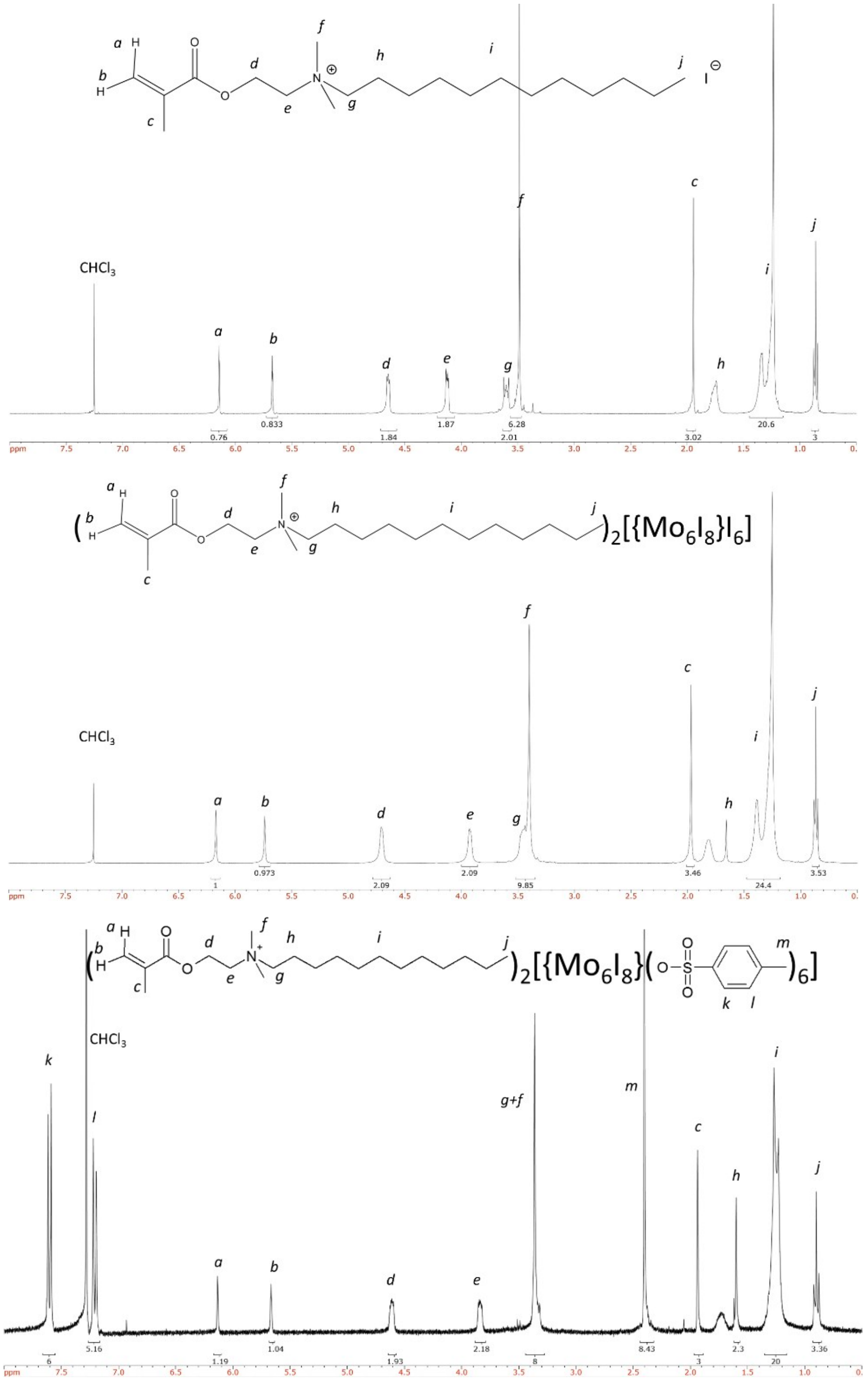


Figure S1. ^{1}H NMR (300.13 MHz) spectra of dMDAEMAI, **1** and **2** with integration in $CDCl_3$. The change of the I^- for $[Mo_6I_8I_6]^{2-}$ leads to significant shielding of CH_2^g and CH_2^e signals, due to the bulkiness of the cluster anion. Substitution of the apical iodide ligands by OTs^- is signified by the appearance of one set of signals of AA'BB' pattern (signals k and l) in the aromatic region and one signal of *para*-CH_3 group (m). This confirms the presence of only one type of the organic ligand in the compound. Notably, hydrogen atoms in the aliphatic chain in the compound **2** are slightly more deshielded than in the compound **1**. This may be explained by van der Waals interactions between the aliphatic chain and the aromatic system of the ligand.

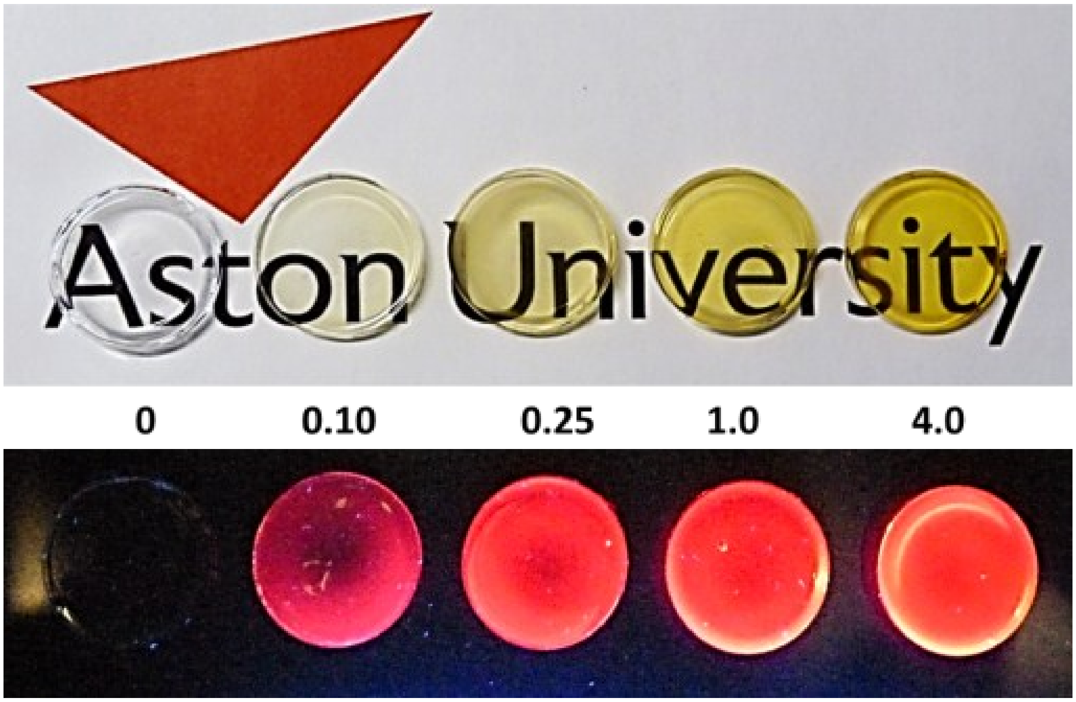
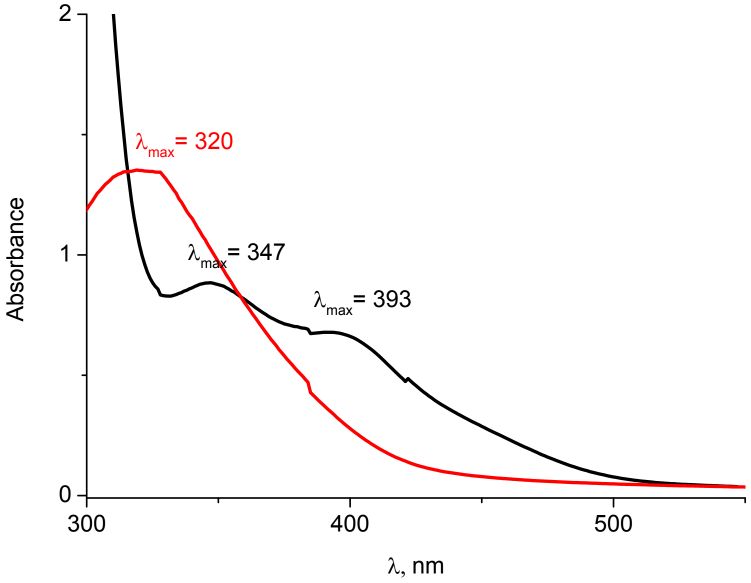
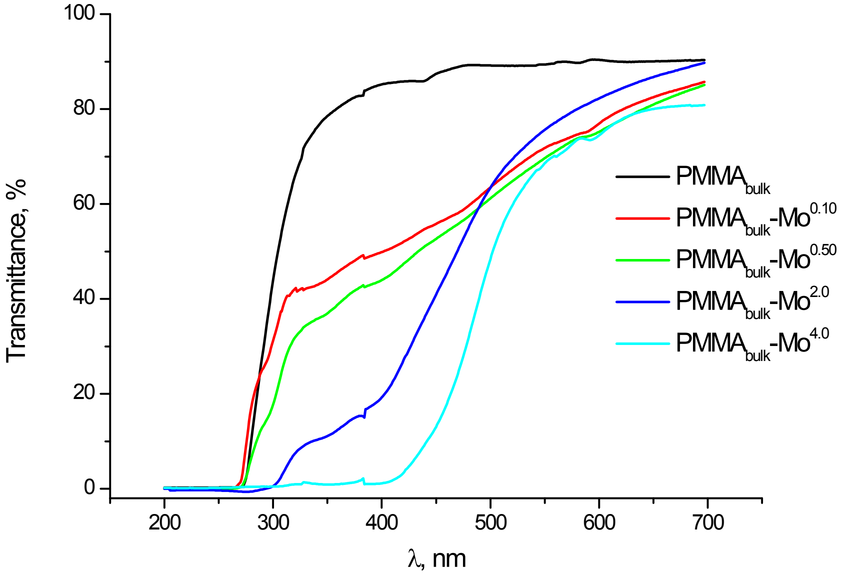


Figure S2. Examples of pellets of $\mathrm{PMMA_{bulk}}$ and $\mathrm{PMMAbulk\text{-}Mo}^{x}$, where x is 0, 0.10, 0.25, 1.0, or 4.0.



a)



b)

Figure S3. a) Absorption spectra of compound **2** in THF: black line - freshly prepared solution and red line the same solution after 12 h of heating at 70 ^{0}C in THF. b) Transmittance spectra of the PMMA$_{bulk}$-Mo^{x} pellets.

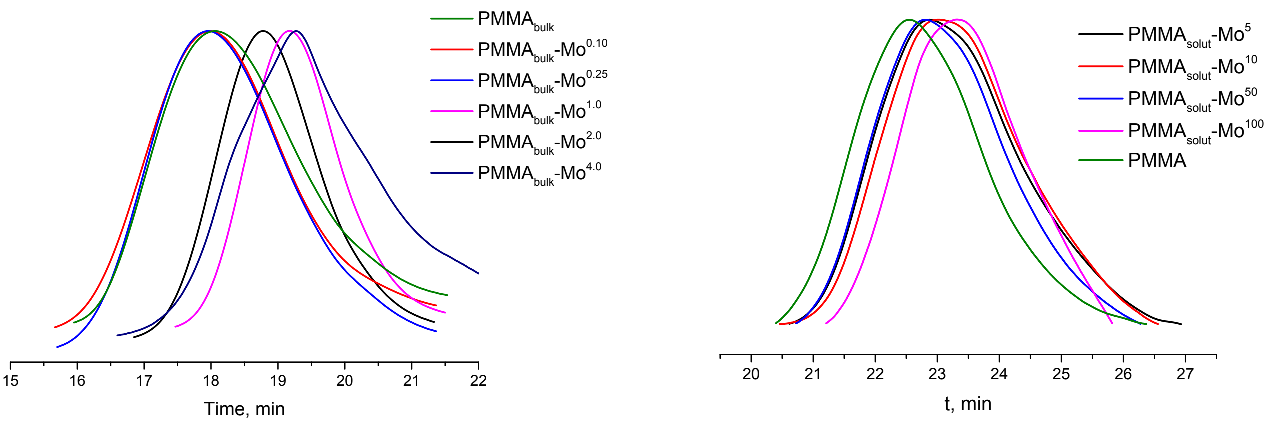


Figure S4. GPC profiles of PMMA$_{bulk}$-Mo^{x} (*left*) and PMMA$_{solut}$-Mo^{x} (*right*) samples.

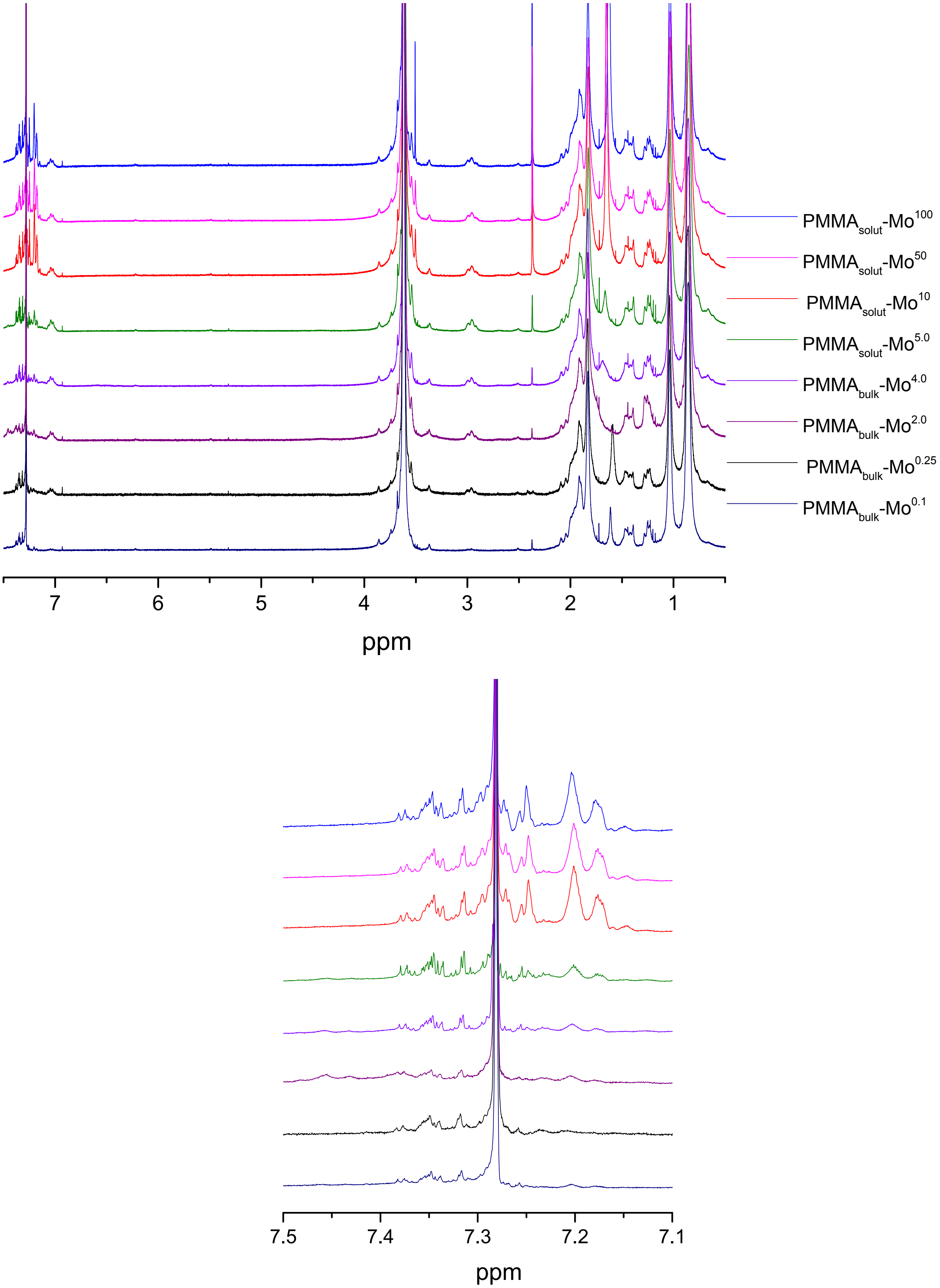


Figure S5. ^{1}H NMR (300.13 MHz) spectra of PMMA$_{bulk}$-Mo^x and PMMA$_{solut}$-Mo^x in CDCl$_3$.

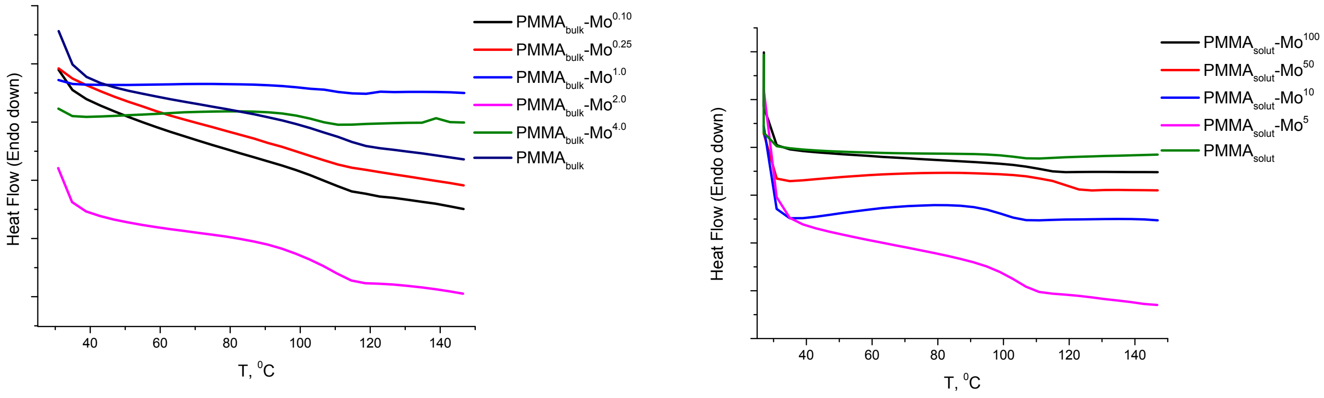


Figure S6. DSC profiles of PMMA$_{bulk}$-Mo^{x} (*left*) and PMMA$_{solut}$-Mo^{x} (*right*) samples. The heating rate was 20˚C/min.

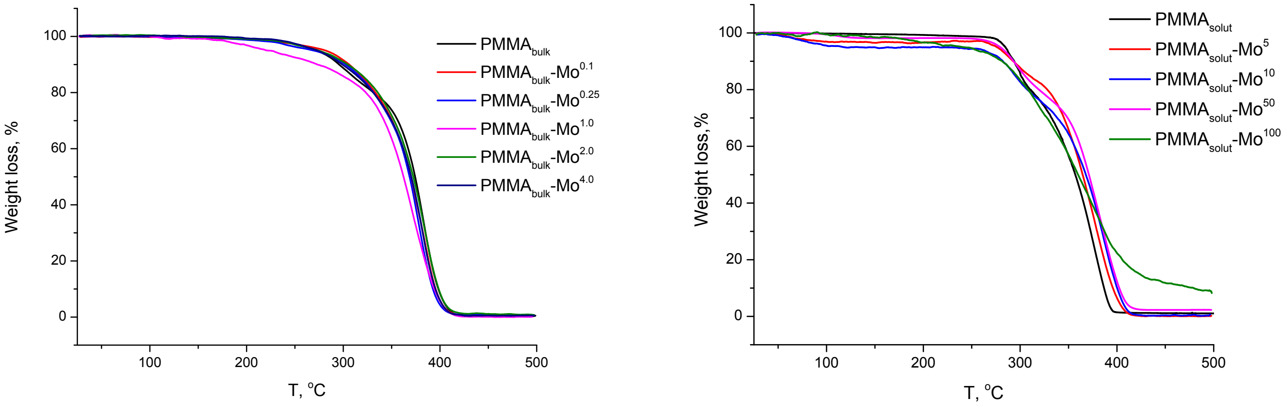
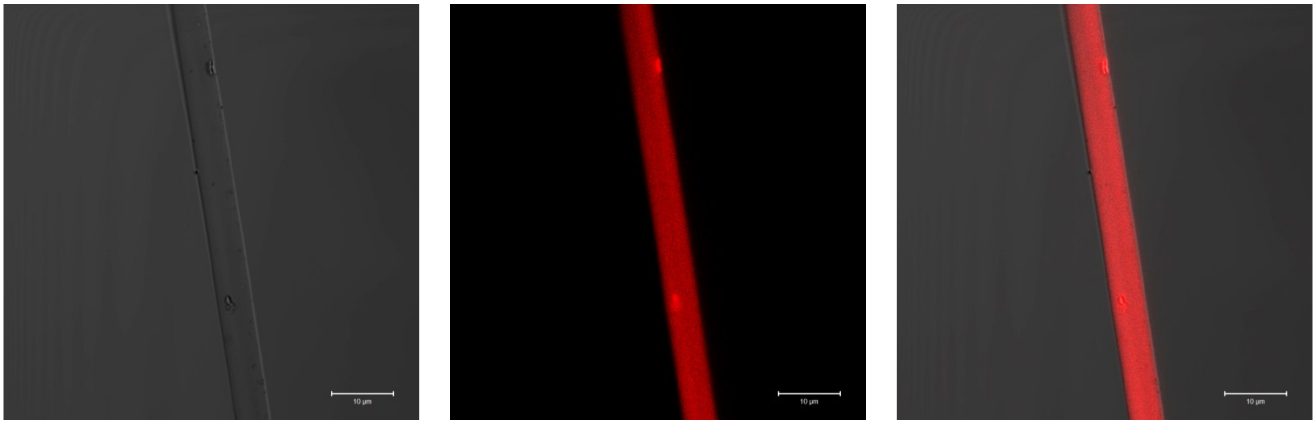


Figure S7. TGA profiles of PMMA$_{bulk}$-Mo^{x} (*left*) and PMMA$_{solut}$-Mo^{x} (*right*) samples.



Optical microscope image | Red luminescence | Merge

Figure S8. Confocal microscopic image of an electrospun fibre of $PMMA_{solut}$-Mo^5.

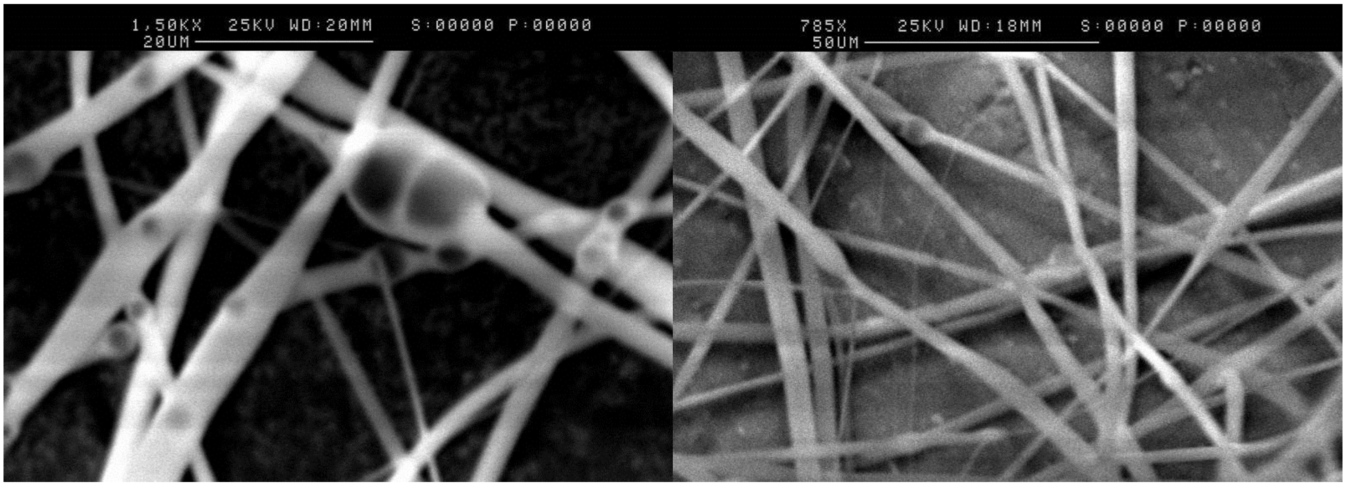
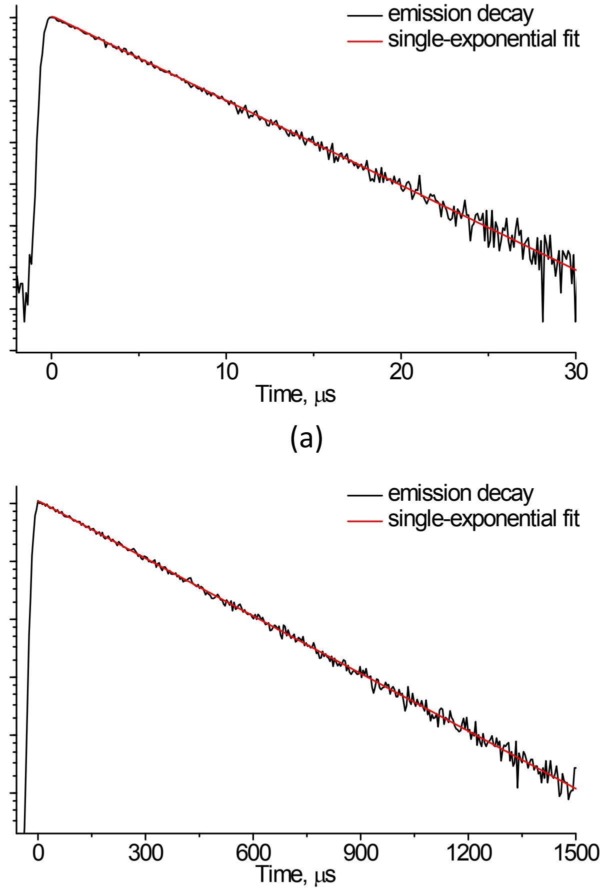


Figure S9. SEM images of $PMMA_{solut}$-Mo^5 sample.

Table S1. The minimum, maximum and average fiber diameters obtained from the electrospinning of 25% chloroform solution of $PMMA_{solut}$-Mo^X

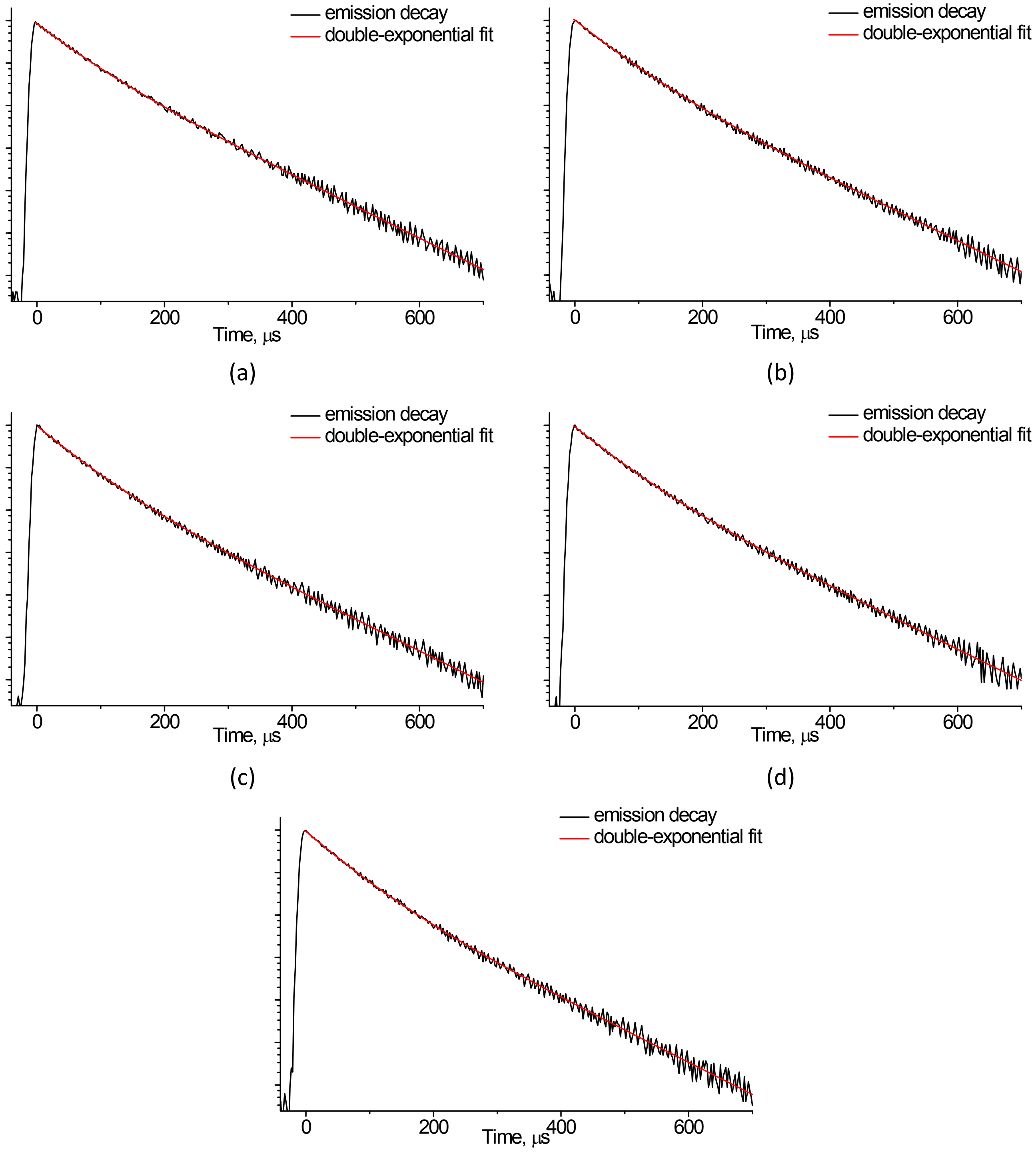
Sample	d_{mean}, μm	SD, μm	d_{min}, μm	d_{max}, μm
$PMMA_{solut}$-$Mo^{5.0}$	3.5	1.3	1.1	7.3
$PMMA_{solut}$-Mo^{10}	3.1	1.1	0.9	6.9
$PMMA_{solut}$-Mo^{50}	3.5	1.5	1.3	10.0
$PMMA_{solut}$-Mo^{100}	3.9	1.4	1.5	9.0



(a)

(b)

Figure S10. The emission decay profiles of **2** in aerated (a) and deaerated (b) acetonitrile solutions. Chi-squared values (χ^2) are 1.15 and 1.09, respectively.



(a)

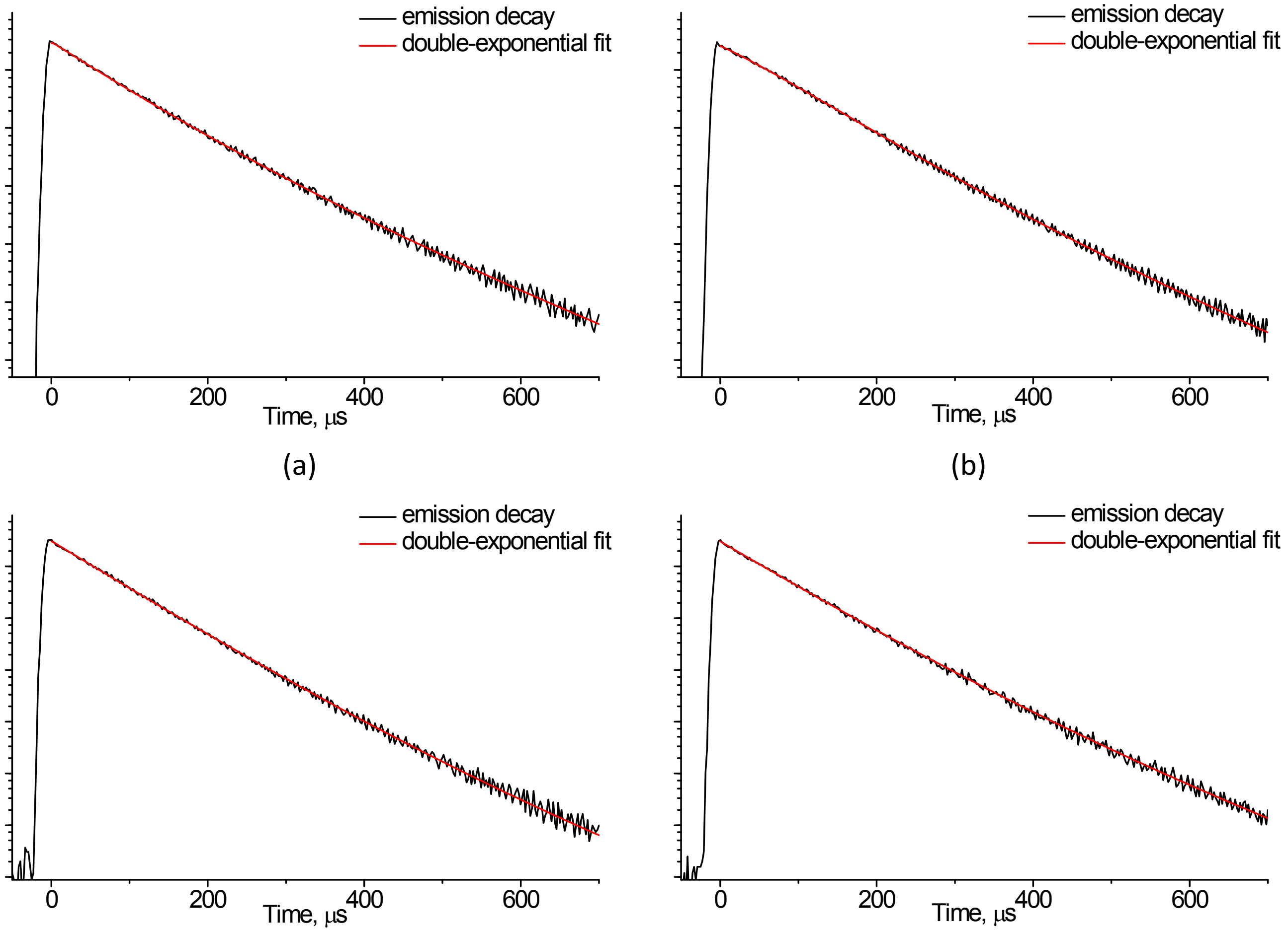
(b)

(c)

(d)

(e)

Figure S11. The emission decay profiles of pelleted bulk polymerised PMMA doped by the cluster complex: PMMA$_{\text{bulk}}$-Mo$^{0.10}$ (a), PMMA$_{\text{bulk}}$-Mo$^{0.25}$ (b), PMMA$_{\text{bulk}}$-Mo$^{1.0}$ (c), PMMA$_{\text{bulk}}$-Mo$^{2.0}$ (d) and PMMA$_{\text{bulk}}$-Mo$^{4.0}$ (e). χ^2 are 1.14, 1.06, 1.15, 1.09 and 1.10, respectively.



(a) (b) (c) (d)

Figure S12. The emission decay profiles of powdered solution polymerised PMMA doped by the cluster complex: PMMA$_{solut}$-Mo$^{5.0}$ (a), PMMA$_{solut}$-Mo^{10} (b), PMMA$_{solut}$-Mo^{50} (c), PMMA$_{solut}$-Mo^{100} (d).
χ^2 are 1.16, 1.13, 1.17 and 1.08, respectively.
PMMA$_{solut}$-Mo^{100} (d).

References

1. G. Pile, K. Kirakci, F. de Montigny, S. P. Cordier, C. Lapinte, C. Perrin and A. Perrin, *Eur. J. Inorg. Chem.*, 2005, 919-928.