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Ruthenium(II) complexes in polymerised bicontinuous microemulsions

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Novel polymerised bicontinuous microemulsions can provide unique microenvironments for some functional molecules of scientific interests and practical applications.

Bicontinuous microemulsion[1,2] consisting of copolymerisable organic components can be used to form integrated transparent polymeric materials possessing bicontinuous nanostructures.[3–5] Using this bicontinuous microemulsion, we have successfully incorporated water-soluble metal complexes such as $[Ru(dip)_3]Cl_2$ (dip = 4,7-diphenyl-1,10-phenanthroline) in the polymerised bicontinuous-cationic-microemulsion.† We have also demonstrated that some environmental changes of the aqueous nanochannels markedly increased the emission intensity of $[Ru(dip)_3]Cl_2$. With such nanostructures, some analytes can readily diffuse reversibly through the aqueous nanochannels to interact with some functional molecules immobilised in the transparent polymer matrix. Our polymerised-microemulsion approach is versatile for producing various nanoporous structures and it can further be developed for sensors and nanocomposites of specific functions.

Fig. 1 shows the remarkable enhancement of luminescence intensity for the polymerised cationic-microemulsion containing $[Ru(dip)_3]^{2+}$ and Fig. 2 the effect of the aqueous content in microemulsion on the triplet metal-to-ligand charge transfer (^{3}MLCT) photoluminescence. The system (Fig. 1) exhibited an enhancement in emission intensity with a blue shift in emission energy (623 nm to 612 nm). The emission lifetime also increased substantially from 0.98 μs (aqueous), 2.0 μs (fluid microemulsion) to 5.8 μs for the polymerised microemulsion.

The substantial increases in emission intensity and lifetime of $[Ru(dip)_3]^{2+}$ are ascribed to rigidochromism resulting from the transformation of dynamic nanostructures of the fluid microemulsion to its solidified state after polymerisation. Such a rigidochromic effect is commonly observed in the excited state of related ruthenium(II) and rhenium(I) polypyridyl systems.[6–10] Upon polymerisation, the emission intensity (emission quantum yield) and lifetime are significantly enhanced, probably as a result of the slower non-radiative decay processes due to the suppressed molecular motion of $[Ru(dip)_3]^{2+}$ in such a rigid environment. In addition, the blue shift in emission energy is also in accord with the rigidochromic effect since the ^{3}MLCT excited state would be less stabilised compared to the case in fluid solution, in which the solvent molecules can effectively rearrange themselves to stabilise the ^{3}MLCT excited state. Similarly, a change in emission intensity of $[Ru(dip)_3]^{2+}$ in polymerised microemulsion has been observed upon progressively decreasing the aqueous content from 40 to 20 wt%. The dependence of emission intensity as a function of aqueous content is also in line with the rigidochromic effect. At lower water contents, the environment can be regarded as more 'rigid' and therefore the emission intensity increases. Thus our method can be used to step-wise modify the microenvironment of metal complexes in polymer matrices at will.

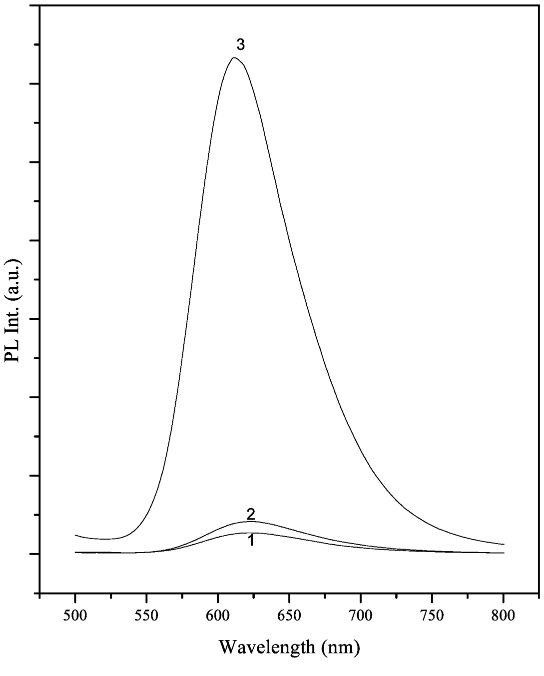

Fig. 1 Emission spectra of $[Ru(dip)_3]^{2+}$ in aqueous solution (line 1), bicontinuous microemulsion containing 30 wt% aqueous solution of 50 μM $[Ru(dip)_3]^{2+}$ before polymerisation (line 2) and after polymerisation (line 3).

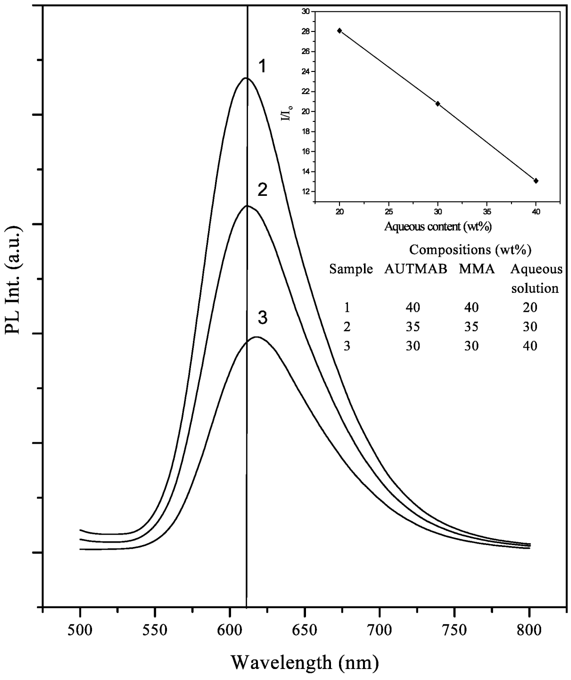

Fig. 2 Emission spectra of $[Ru(dip)_3]^{2+}$ in polymerised microemulsion showing the effect of aqueous content. The insert shows the changes in maximum luminescence intensity of $[Ru(dip)_3]^{2+}$ in polymerised microemulsions at the same amount of $[Ru(dip)_3]^{2+}$ but with various aqueous contents.

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Furthermore, the fluorescence of $[Ru(dip)_3]^{2+}$ can largely be quenched within 5–10 min by a dilute (several ppm) aqueous solution of potassium ferrocyanide as shown in Fig. 3. Since the polymerised bicontinuous-microemulsion has nanoporous open structures, water and $[Fe(CN)_6]^{4-}$ ions can freely and rapidly pass through the nano-channels of the polymer network. The strong electrostatic attractions between the negatively charged $[Fe(CN)_6]^{4-}$ and the positively charged surfactants along water–polymer interfaces facilitates effective interactions with bound $[Ru(dip)_3]^{2+}$ molecules in the polymerised bicontinuous-cationic-microemulsion film. The use of a polymerised bicontinuous-cationic-microemulsion as a matrix allowed $[Ru(dip)_3]^{2+}$ complexes to be immobilised resulting in its good sensitivity and fast response to the quencher from the external phase. We believe that our novel polymerised bicontinuous-microemulsions with nanoporous structures are applicable to many other systems and they hold promise for many applications, such as chemical sensors and biosensors.

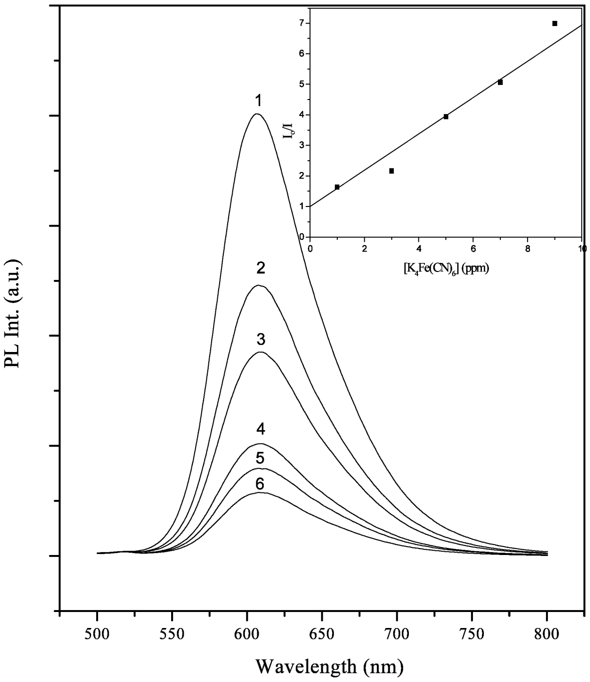

Fig. 3 The effect of potassium ferrocyanide on luminescence spectra of $[Ru(dip)_3]^{2+}$ in polymerised cationic microemulsion (sample 2 as in Fig. 2): (1) 0 ppm, (2) 1 ppm, (3) 3 ppm, (4) 5 ppm, (5) 7 ppm and (6) 9 ppm. The contact time between the potassium ferrocyanide solution and the polymer film was 10 min. The insert is the Stern–Volmer plot for quenching of $[Ru(dip)_3]^{2+}$ by potassium ferrocyanide.

Notes and references

† *Experimental*: the cationic bicontinuous microemulsion consisting of polymerisable cationic surfactant of acryloyloxyundecyltrimethylammonium bromide (AUTMAB), methyl methacrylate (MMA), an aqueous solution of 50 μM $Ru(dip)_3Cl_2$ (dip = 4,7-diphenyl-1,10-phenanthroline), crosslinker ethyleneglycol dimethacrylate (EGDMA) and free-radical initiator 2,2′-azobisisobutyronitrile (AIBN) was polymerised at 65 °C. The compositions of some microemulsions are listed in Fig. 2.

Steady-state luminescence spectra were recorded on a Perkin-Elmer LS-50B fluorespectrometer, equipped with a 7.3 W pulsed Xenon discharge lamp, average power at 50 Hz, with the excitation wavelength of 460 nm. Emission lifetime measurements were made using a conventional laser system. The excitation source was the 355 nm output (third harmonic) of a Quanta-Ray Q-switch GCR-150-10 pulsed Nd:YAG laser and the decays were monitored at 610 nm. Luminescence decay signals were recorded on a tektronic TDS 620A digital oscilloscope and analysed using a program for exponential fit to the equation $I(t) = I_o\exp(-t/\tau)$, where $I(t)$ stands for emission intensity at time t after the laser pulse, τ is the luminescence decay time and I_o is the initial intensity at $t = 0$.

Quenching of $[Ru(dip)_3]^{2+}$ emission by potassium ferrocyanide ($K_4[Fe(CN)_6]$) in polymerised microemulsion was determined by emission intensity measurements. The polymerised microemulsion films equilibrated with well-stirred $K_4[Fe(CN)_6]$ solution (1–9 ppm) for 10 min were found to reach the respective maximum quenching. Prior to measurements, the film was rinsed with distilled water and it was then sandwiched between two quartz slides for the emission measurement.

1 W. Jahn and R. Strey, *J. Phys. Chem.*, 1998, **92**, 2294–2301.
2 P. Pieruschka and S. Marcelja, *Langmuir*, 1994, **10**, 345–350.
3 F. Candau and J. Y. Anquetil, in *Micelles, Microemulsions and Monolayers*, ed. D. O. Shah, Marcell Dekker, New York, 1998, 193–213.
4 C. H. Chew, L. M. Gan, L. H. Ong, K. Zhang, T. D. Li, T. P. Loh and P. M. MacDonald, *Langmuir*, 1997, **13**, 2917–2921.
5 C. H. Chew, T. D. Li, L. H. Gan, C. H. Quek and L. M. Gan, *Langmuir*, 1998, **14**, 6068–6076.
6 R. J. Lin, T. Onikubo, K. Nagai and M. Kaneko, *J. Electroanal. Chem.*, 1993, **348**, 189–199.
7 M. Kaneko, S. Iwahata and T. Asakura, *J. Photochem. Photobiol. A*, 1991, **61**, 373–380.
8 M. Kaneko and S. Hayakawa, *J. Macromol. Sci. Chem.*, 1988, **A25**, 1255–1261.
9 K. Rajeshwar and M. Kaneko, *Langmuir*, 1989, **5**, 255–260.
10 A. J. Lees, *Comments: Inorg. Chem.*, 1995, **17**, 319–346.