Coordination-Driven Modulation of Chiroptical Properties in Terpyridine-Functionalized Supramolecular Gel Assemblies

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Supramolecular metal complexes exhibit unique optical, electronic, and magnetic properties, making them promising candidates for applications in various advanced materials and devices. We have previously reported the circular polarization properties of supramolecular gels derived from molecules containing a dialkylated glutamide (G) unit, as well as their tunability through external stimuli. The G unit promotes the formation of supramolecular gels via intermolecular hydrogen bonding, which can induce significantly enhanced circular polarization properties due to the chiral orientation of chromophores linked to the G unit through covalent or non-covalent interactions. Supramolecular gels formed from G-linked ligand molecules exhibit significant changes in their circular polarization properties upon coordination with metal ions [1–3].

Here, we demonstrate the modulation of circular polarization properties in supramolecular gels formed from a G-linked terpyridine (G-tpy) [3] by complexation with various metal ions, followed by coordination with achiral guest ligands. Upon addition of metal ions to G-tpy in a 1:1 molar ratio in a cyclohexane/ethanol (9:1) solvent system, enhanced circular dichroism (CD) and circularly polarized luminescence (CPL) signals were induced, whereas almost no signals were observed in the absence of metal ions. These CD and CPL signals appeared near the absorption bands and emission wavelengths of the metal–G-tpy complexes, respectively, with both intensity and spectral pattern strongly dependent on the metal ion used.

Furthermore, the addition of achiral guest ligands induced notable changes in the CD and CPL spectra. When an equimolar amount of 2,2':6',2''-terpyridine (Tpy) was added to the G-tpy complex with Zn^{2+} (G-tpy(Zn)), a significant enhancement in the CD spectra accompanied by a red shift in absorption was observed (Fig. 1). Interestingly, the CPL signal of G-tpy(Zn) exhibited a sign reversal upon addition of Tpy. The aggregate morphology of G-tpy also changed dramatically from fibrous to plate-like aggregates upon addition of Zn^{2+}, and reverted to fibrous structures after addition of Tpy.

Keywords:
Self-assembly, Circularly polarized luminescence (CPL), Nano-fibrous aggregates, Metal ion complex

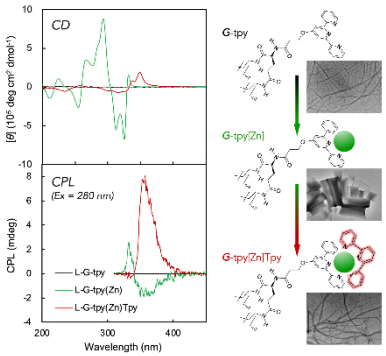

Fig. 1 CD and CPL spectra, and TEM images of G-tpy, G-tpy(Zn) and G-tpy(Zn)Tpy.

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