Chirality

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Circularly Polarized Luminescence of Rhodamine B in a Supramolecular Chiral Medium Formed by a Vortex Flow**

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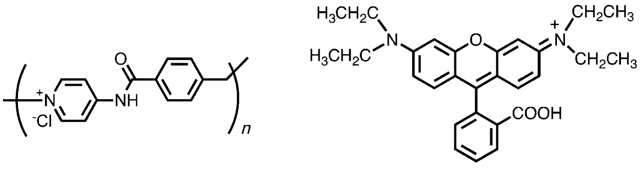
Circularly polarized light is inherently chiral and has been regarded as one source for the origin of homochirality.[1] Circularly polarized luminescence (CPL) inevitably requires helically arranged luminophores. Typically, this luminescence can be generated when a luminophore exists in a dissymmetric environment in the photoexcited state. In fact, several photoluminescent π-conjugated polymers that bear enantiopure side-groups in the film state can induce CPL with a considerably high Kuhn dissymmetry ratio (g_{lum}).[2] Chen et al. reported an almost ideal CPL amplitude ($g_{\mathrm{lum}} \approx -1.8$) of achiral photoluminescent oligofluorene (Exalite 428) as a guest by doping a cholesteric liquid crystal (ChLC) film as a chiral host, although the CPL sign was limited to negative because of the inherent handedness of the host material.[3b] Brett and co-workers reported the CPL of an achiral luminophore (Alq_3; tris(8-hydroxyquinolinato)aluminium) embedded in a chiral sculptured inorganic film fabricated by the glancing-angle deposition (GLAD) technique.[4] The chirality of the film and the sign of the CPL of Alq_3 may be controlled by switching the rotation direction of the GLAD equipment. Herein we demonstrate that the physical chirality of a vortex flow[5] is transferred to the CPL by using a mechanochiral system.

Compared to these stable helical nanoarchitectures, a stir-induced vortex is regarded as spatiotemporal spiral architecture on a macroscopic level. Stir-induced circular dichroism (CD) has previously been reported for a solution containing supramolecular assemblies of porphyrins in water.[6,7] The effect has been interpreted as an instrumental artifact that arises from the combination of linear dichroism and birefringence of the aligned particles around the vortex.[7] However, Mueller matrix polarimetry shows that true CD signals arise when the stir-induced torque leads to the folding or torsion of particles.[8] Moreover, a chiral symmetry breaking was demonstrated in a lyotropic liquid crystal system by using polarizing optical microscopy.[9] We also recently reported that a stir-induced chiral influence arising from a synthetic oligomer (**1**; Scheme 1) as an achiral ionic host is transferable to an absolutely achiral dye as a guest molecule in aqueous solution.[10] Based on these results, we assumed that an achiral luminophore embedded into a stir-induced chiral system should show a CPL effect in which the CPL sign as well as the stir-induced CD effect is controlled solely by the stir direction. Herein we report novel media that display CPL and can be produced within one hour by a stir-induced vortex flow with the use of an achiral green luminescent dye (Rhodamine B, **2**) incorporated into **1**.



Host gelator: **1**

Guest luminophore: Rhodamine B **(2)**

Scheme 1. Molecular structure of the ionic oligomer (**1**) and luminophore dopant (Rhodamine B, **2**).

At a low concentration (0.6 wt %) of **1**, the sample formed a very soft gel that shows stir-induced thixotropy at room temperature, that is, a gel–sol phase transition occurred by employing stirring only. The gel–sol transition of the 0.6 wt % solution of **1** occurred at 73–75 °C and is responsible for the production of chiral supramolecular structures. In fact, no CD signal was observed when **1** was stirred in the sol phase above 75 °C.

We initially examined stir-induced CPL behavior of **2** (1.6×10^{-5} M) in an aqueous solution of **1** (0.6 wt %; Figure 1). When the solution was not stirred, a very weak CPL signal that arises from an element of linearly polarized luminescence was observed. On the other hand, a CPL signal in the same wavelength region as the photoluminescence was observed upon mechanical stirring at 1000 rpm (Figure 1 b); this handedness can be tuned by changing the rotational direction. Furthermore, when the stirring was stopped, the CPL signal of the solution was no longer observed. Based on these results, we consider that a more rigid gel is suitable for inducing and fixing the stir-induced optical activity.

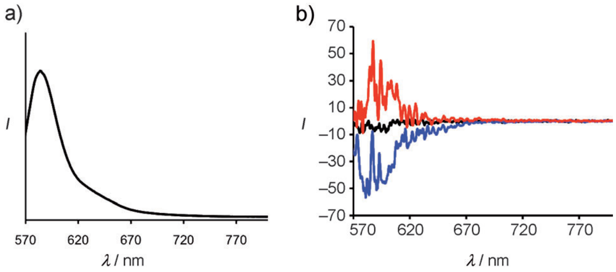


Figure 1. a) Photoluminescence spectra (PL) spectra ($\lambda_{\mathrm{ex}} = 520$ nm) of **2** (1.6×10^{-5} M) in an aqueous solution of **1** (0.6 wt%). b) Circularly polarized luminescence spectra (CPL) of the solution with clockwise (CW, red) and counterclockwise (CCW, blue) stirring at 1000 rpm, and unstirred (black). For CPL spectroscopy, a beam of incoherent unpolarized excited light (Ø = 5.0 mm) passed through the sample solution 3 mm above the center of the stir bar.

We subsequently designed a CPL-active hydrogel (Figure 2 a). Firstly, a mixture of an aqueous solution of **1**

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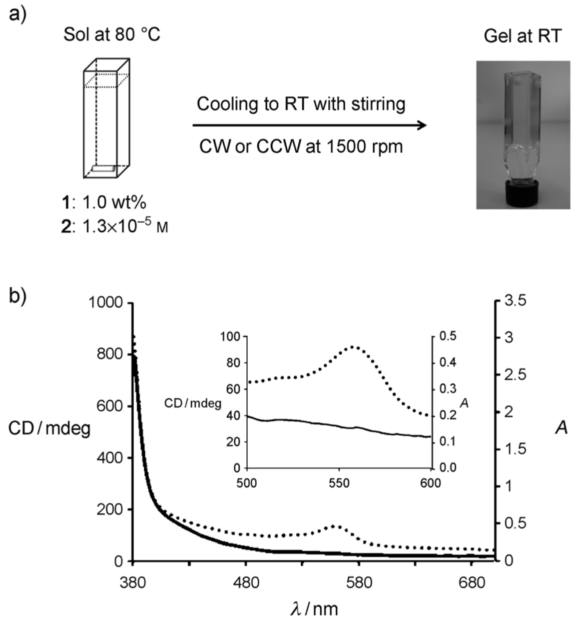

Figure 2. a) Preparation of hydrogels used in this study. A sample solution was placed in a 10×10×40 mm^3 quartz optical cell containing a 2.0×5.0 mm^3 magnetic stirring bar at the bottom. The gels were prepared by cooling of sols at 80 °C with clockwise (CW) or counter-clockwise (CCW) stirring at 1500 rpm. b) Absorption (dotted line) and circular dichroism (CD; solid line) spectra of the hydrogel composed of **1** (1.0 wt %) and Rhodamine B (1.3×10^{-5} M). Inset: enlargement of the spectra between 500 and 600 nm.

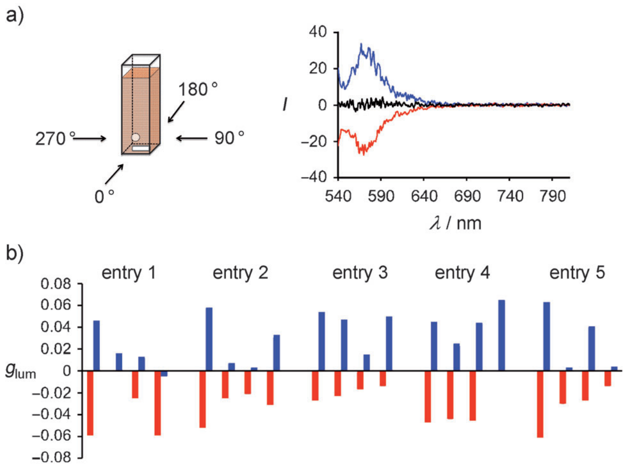

Figure 3. a) Circularly polarized luminescence (CPL) of the hydrogels of **2** (1.6×10^{-5} M) in an aqueous solution of **1** (0.6 wt %) prepared with clockwise (CW, red) and counterclockwise (CCW, blue) stirring, and no stirring (black). For CPL spectroscopy, a beam of incoherent unpolarized incident light (Ø = 5.0 mm) passed through the sample solution 3 mm above the center of the stir bar. b) To evaluate statistical distributions, multiple measurements of four different faces were employed. Statistical distributions of g_{lum} values in five different samples prepared by CW (red) and CCW (blue) operations in four faces of the sample cuvette. All original data are given in the Supporting Information.

(ca. 1.0 wt %) and **2** (1.3 × 10^{-5} M) was prepared, followed by gradual heating to the sol phase at 80 °C. The stirring speed and direction were maintained and the mixture allowed to gradually cool to room temperature in order to imprint a certain chirality into the gel of **1**. The sample gel for CPL study was prepared in a 10 × 10 × 40 mm^3 quartz cuvette, in which the solution was mechanically stirred with a 2.0 × 5.0 mm^3 Teflon-coated magnetic stir bar. The CD spectrum of the gel showed the intense Cotton signal of **1**, which is similar to the corresponding unpolarized UV/Vis absorption bands that arise from the π–π* transition around 390 nm (Figure 2 b). This optical activity was preserved at room temperature for at least one year. On the other hand, a scattering signal may induce minimal contribution to the CD signal of **2**. This observation led to the conclusion that the stir-induced CD signal of **2** could be embedded in that of the ionic oligomer.

The stir-induced **2**-doped gels gave almost mirror-image CPL spectra in which the sign of the signal was determined by the stir direction (Figure 3 a): a positive sign was induced with counterclockwise (CCW) stirring, conversely, a negative sign was induced with clockwise (CW) stirring. The spectral shapes of the prominent CPL signals are almost identical to the corresponding PL spectra and show a maximum at around 580 nm. The sign of the CPL spectrum of **2** in the excited state is consistent with that of sign of the CD signal of **1** at 390 nm in the ground state (see the Supporting Information). The stir-induced chiral influence in the host gel is assumed to transfer to the helical alignment of **2** on a molecular level. For comparison, the gel formed without any stirring did not give any spectral features. When the temperature of the sample increases above the sol–gel transition temperature, the stir-induced CPL signal disappeared and the photoexcited chiral information was erased because of dissociation of the supramolecular structures into the solution. The reformation of the chiral gel phase was shown to be possible because similar CPL spectra of **2** reappeared by the same chiroptical generation procedure. This is the first example of a dye-doped smart gel that exhibits CPL properties and is capable of a reversal in the sense of the CPL driven by external stimuli. Thus the present simple stir-induced gel formation process above and below the gel–sol transition temperature will allow a desired CPL sign of various doped photoluminescent dye molecules to be formed and erased.

To conclusively verify the origin of the CPL spectra, we recorded measurements through the four different faces of the cuvette containing the **2**-doped gel (Figure 3 c).[6c] The CPL signal intensities at 577 nm at each face are somewhat different. The stir-induced optical activity in the cuvette is case-dependent for several reasons,[5d,6] and the stirring and probing position, stir rate, and cuvette shape may considerably affect the nature of vortex flow. Subtle deviations in cooling rate and stir position in the cuvette may result in a statistical distribution of the CPL amplitude and sign. However, spectra recorded through the four different faces showed a similar shape with the same sign in a series of CPL measurement experiments, although the CPL magnitude is somewhat dependent on the face through which the spectrum is recorded. These results support the hypothesis that the stir-induced chirality on a macroscopic level is transferable to **2**. The vortex flow with chiroptical sense by stir-induced **1**-based sol makes it possible for achiral **2** molecules to arrange into a spatiotemporally helically organized structure and to persistently immobilize the chiral information to the gel through the stirring and cooling process.[11]

To quantify the observed CPL data, the g_{Lum} value is defined as $g_{\mathrm{lum}} = 2(I_L - I_R)/(I_L + I_R)$, where I_L and I_R are the output signals for left and right circularly polarized light.[12] Experimentally, the g_{lum} value was evaluated as $\Delta I/I =$ (ellipticity/(32980/ln10))/(unpolarized PL intensity) at a CPL extremum wavelength. The maximum g_{lum} value ranges from $+2$ for an ideal left CPL and -2 for an ideal right CPL. The first report of the efficient generation of CPL from a luminophore-doped ChLC gave $g_{\mathrm{lum}} = 0.3$ at an off-resonance region.[13] The greatest g_{lum} value of -1.8 was achieved in the well-designed Exalite 428-doped ChLC by using a selective reflection mode.[3b] The most typical $|g_{\mathrm{lum}}|$ values for chiral π-conjugated polymer thin films and supramolecular aggregates range from 10^{-3} to 10^{-2}.[2,14] To enhance the $|g_{\mathrm{lum}}|$ value to approximately 0.2, a prolonged thermal annealing process of the pristine chiral polymer films is further required.[2a] More recently, Nakano and co-workers reported an optically active, π-conjugated hyperbranched polymer film that exhibited a very high g_{lum} value of -0.45 at 430 nm without annealing process that leads to a main-chain helical ordering.[15] Helically aligned $\mathrm{Alq_3}$ incorporated into a chirally sculptured inorganic film had a $|g_{\mathrm{lum}}|$ value of 0.30.[4] The greatest g_{lum} value of the **2**-doped **1**-based hydrogel in our system was ± 0.06 at 577 nm.

In summary, we have demonstrated a novel CPL emissive system that is established by a stir-induced vortex. The host gelator is useful for this system because, as previously reported, compound **1** is readily obtained by a one-pot synthesis with commercially available reagents and the gel is composed of around 99 % water.[16] The uniqueness of the **2**-doped gel reported in this study was that 1) control between the positive and negative signs of CPL is possible by switching only the vortex direction, 2) the induced CPL signal that originates from **2** is erasable upon heating and/or nonstirred cooling runs, and 3) various water-soluble luminescent dyes that cover the UV to near-infrared region, including **2**, may be utilized in the future. This is the first example of how the sense of a macroscopic vortex flow can determine the optically active state of a gel, and how the transfer of chiral information from the stir direction to molecular chirality can be confirmed by probing the molecular CPL signal of the gel.

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