# ChemComm

## COMMUNICATION

# Chirality-switchable Circularly Polarized Luminescence in Solution Based on the Solvent-dependent Helix Inversion of Poly(quinoxaline-2,3-diyl)s

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Poly(quinoxaline-2,3-diyl)s containing (S)-2-methylbutoxy side chains were found to exhibit blue circularly polarized luminescence (CPL). The handedness of the CPL could be switched by a solvent-dependent helix inversion of the polymer backbone between chloroform (*M*-helical structure) and 1,1,1-trichloroethane (*P*-helical structure).

Circularly polarized luminescence (CPL)[1] is defined as the differential emission of right- and or left-handed circularly polarized light. CPL has attracted considerable interest in the past, not only due to its capacity to elucidate chiral structures in the excited state,[2] but also because of potential applications in chemical sensors,[3] biological probes,[4] and three-dimensional displays.[5] Much effort has been devoted to the development of CPL materials based on small chiral molecules[6] and helical macromolecules[7] in aggregates or the solid state. Examples of materials exhibiting CPL in a non-aggregated state, on the other hand, still remain limited, despite the expectation of the development of CPL materials operating in solution. To date, chiral lanthanide complexes,[8] sterically strained π-conjugated compounds,[9] and supramolecules exhibiting intramolecular excimer emission[10] have been described as examples of non-aggregated CPL materials. Recent research interest has focused on the switch of the CPL handedness, for example by using achiral external stimuli[11] such as solvent,[12] non-polarized light,[13] or an achiral matrix.[14] However, only few examples exhibit an inversion of CPL chirality in aggregates or the solid state, and no example of CPL inversion in dilute solution has been reported yet.

Recently, we reported the solvent-dependent switch of helical chirality in poly(quinoxaline-2,3-diyl) containing chiral side chains using either chloroform (CHCl3, >99% se, *P*-helix) or 1,1,2-trichloroethane (1,1,2-TCE, >99% se, *M*-helix) as solvents.[15] We also demonstrated that poly(quinoxaline-2,3-diyl)s bearing diarylphosphino groups can serve as highly effective chiral supporting ligands for transition metal catalysts in various asymmetric reactions.[16] The chirality of these catalysts can be inverted in a controlled fashion by the choice of solvent, resulting in the formation either *R*- or *S*-enantiomers with high levels of

enantiomeric excess. Herein, we report the dependence of the CPL emission of poly(quinoxaline-2,3-diyl)s on the helical sense of the polymer backbone, which can be controlled by solvent effects.

Firstly, we measured the UV-vis absorption of 200mers **1(200)**, **2(200)**, and **3(200),** as well as of monomeric model compound **4** in CHCl3 (Figure 1A). All compounds showed similar bimodal absorption peaks arising from the π-π* transition of the quinoxaline ring. Photoluminescence (PL) spectra of **1–4** showed that these compounds also exhibit blue fluorescence emission (Figure 1B). The PL intensity of polymer **3(200)** with alkoxy side chains was significantly stronger than that of **1(200)** and **2(200)**, where the chiral side chains are connected via a carbon atom. Absolute fluorescence quantum yields for **1(200)** and **2(200)** in CHCl3 solution were found to be 0.3%, and 0.7% for **3(200)**. Even though these fluorescence quantum yields were low, the fluorescence emission could still be observed visually (Figure 1D), due to the large molar absorption coefficients (log $\varepsilon$ = 3.97 at 365.0 nm per monomer unit). The significantly stronger fluorescence of polymer **3(200)** relative to **1(200)** and **2(200)** may be explained by the increased electron donating ability of the alkoxy groups, which are directly attached to the electron-deficient quinoxaline ring. Polymer **3(200)** exhibited a broader emission peak compared to model compound **4**, probably due to excitonic interactions between quinoxaline rings. Circular dichroism (CD) spectra of polymers **1(200)**, **2(200)**, and **3(200)** clearly showed a Cotton effect, reflecting their previously reported helical main chain (Figure 1C). On the other hand, the CD spectrum of model compound **4** did not show any peaks, corroborating that the CD peaks of the polymers **1-3** originate exclusively from the helical arrangement of the quinoxaline rings.
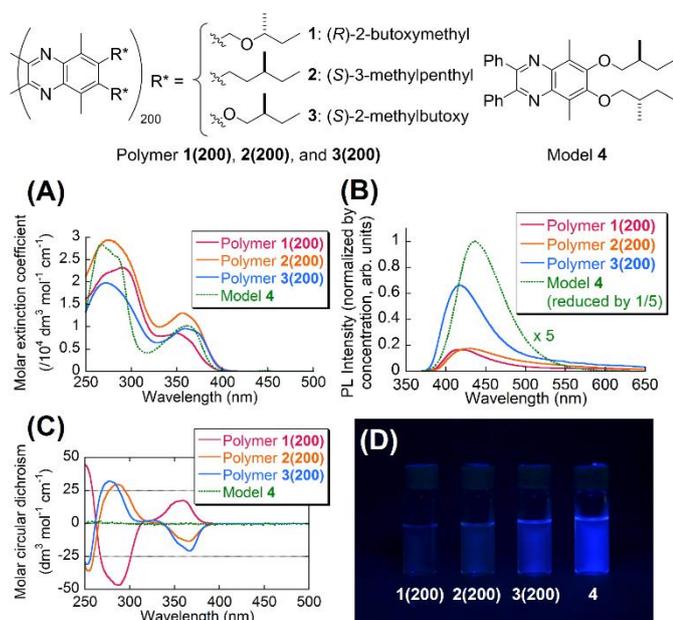
**Figure 1.** (A) UV-absorption, (B) PL, and (C) CD spectra of polymers **1(200)** ($4.9 \times 10^{-5}$ M), **2(200)** ($7.3 \times 10^{-5}$ M), **3(200)** ($6.5 \times 10^{-5}$ M), and monomeric model compound **4** ($1.0 \times 10^{-5}$ M) in CHCl$_3$. (D) Photograph of **1-4** in CHCl$_3$ ($1.0 \times 10^{-5}$ M) under UV light irradiation ($\lambda_{ex} = 365$ nm).

We then became interested in the solvent-dependent helix inversion of polymer **3**. As discussed in our previous paper,[15b] polymeric 40mer **3(40)** adopted an *M*-helical conformation in CHCl$_3$ and a *P*-helical conformation in 1,1,2-TCE. Unfortunately, polymers of **3** with higher molecular weight (100mer and 200mer) were insoluble in 1,1,2-TCE. Experimenting with different solvents, we found that 1,1,1-trichloroethane (1,1,1-TCE) was both able to cause the solvent-dependent helix inversion of polymer **3** and dissolve the 100mer and 200mer. In order to determine the gained energy difference per monomer unit ($\Delta G_h$) and the dissymmetry factor $g_{abs}$ for the purely single-handed helical structure ($g_{max}$) in CHCl$_3$ and 1,1,1-TCE, we prepared seven polymers with (*S*)-2-methylbutoxy side chains and different degrees of polymerization (30–200mer). All polymers exhibited *M*-helical structures in CHCl$_3$ and *P*-helical structures in 1,1,1-TCE. In accordance with Green's theory,[17] the screw-sense excesses (se) increased in a non-linear fashion in parallel to increased degrees of polymerization (Figure 2A). The $g_{max}$ values at 366.0 nm were found to be $-2.29 \times 10^{-3}$ (CHCl$_3$) and 1.55 $\times 10^{-3}$ (1,1,1-TCE), both of which are comparable to previously reported polymer systems.[15b] Values for $\Delta G_h$ were found to be 0.07 kJ/mol (CHCl$_3$) and 0.14 kJ/mol (1,1,1-TCE).[18] These results indicate that **3(200)** adopted at room temperature exclusively (>99% se) *P*- or *M*-helical conformations in CHCl$_3$ or 1,1,1-TCE, respectively. The CD spectra of **3(200)** in CHCl$_3$ and 1,1,1-TCE were almost perfect mirror images of each other, indicating almost absolute solvent-dependent helix inversion between these two
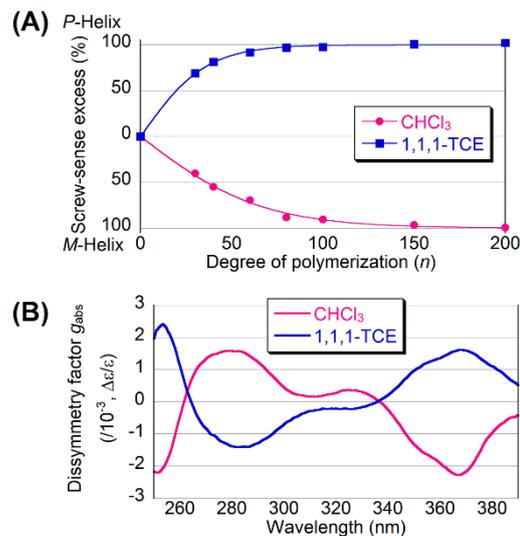
solvents (Figure 2B).



**Figure 2.** (A) Correlation between the degree of polymerization *n* and the screw-sense excess (*se*) of the polymers **3(*n*)** (*n* = 30, 40, 60, 80, 100, 150, and 200) in CHCl$_3$ and 1,1,1-TCE. (B) CD spectra of **3(200)** in CHCl$_3$ and 1,1,1-TCE.

Finally, we measured the CPL of **3(200)** in dilute solutions of several organic solvents including CHCl$_3$ and 1,1,1-TCE (Figure 3, for spectra in other solvents, see SI). Indeed, CPL signals of **3(200)** could be observed even in dilution, indicating that the signals observed stem from the helical conformation of the quinoxaline rings. We also confirmed that the concentration of the solutions did not affect the UV, CD, PL, and CPL spectra in the range of $1.3 \times 10^{-5}$ to $3.2 \times 10^{-4}$ M (see SI). Again, these CPL signals were almost identical mirror images of each other. The CPL dissymmetry factor $g_{lum}$ is defined as $g_{lum} = 2(I_L - I_R)/(I_L + I_R)$, where $I_L$ and $I_R$ are the fluorescence intensities of the right- and left-handed circularly polarized light, respectively. Maxima for $|g_{lum}|$ were found at $2.3 \times 10^{-4}$ (CHCl$_3$) and $4.1 \times 10^{-4}$ (1,1,1-TCE), which are comparable with previously reported non-switchable CPL materials in solutions (typical $|g_{lum}| = 10^{-5}–10^{-2}$).[9d] The dissymmetry factors of absorbance ($g_{abs}$) can be obtained from CD and UV spectra and were found to be 10 and 3.8 times larger than the corresponding $g_{lum}$ values in CHCl$_3$ and 1,1,1-TCE, respectively. It should be noted that polymers **1(200)** and **2(200)** also showed CPL peaks in CHCl$_3$, although model compound **4** did not exhibit any CPL in CHCl$_3$ or 1,1,1-TCE (see SI), further confirming that the CPL emission of **3(200)** originated solely from the helical alignment of the quinoxaline rings.
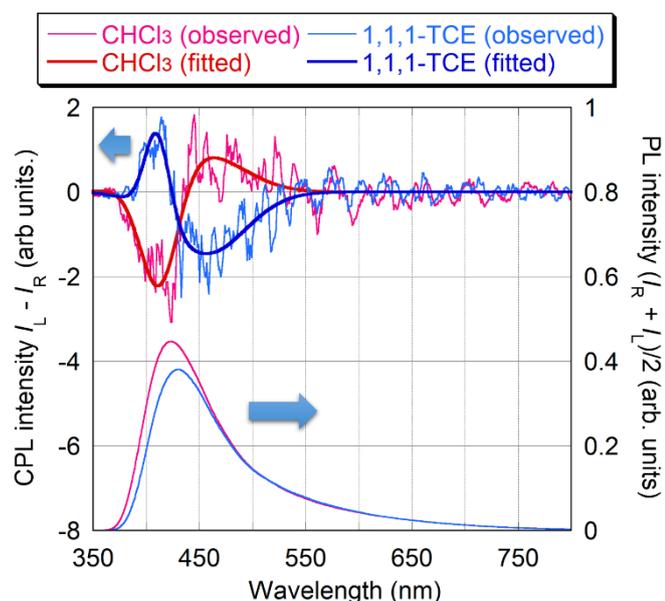
**Figure 3.** CPL and PL spectra of **3(200)** in dilute ($9.1 \times 10^{-5}$ M) CHCl$_3$ and 1,1,1-TCE solutions ($\lambda_{ex}$ = 300.0 nm).

In summary, we have investigated the photoluminescence properties of single-handed helically chiral poly(quinoxaline-2,3-diyl)s containing chiral side chains in CHCl$_3$ and 1,1,1-TCE. A polymer containing (*S*)-2-methylbutoxy side chains unambiguously showed a solvent-dependent helix inversion between a purely *P*-helical structure in CHCl$_3$ and a purely *M*-helical structure in 1,1,1-TCE. The polymer moreover exhibited solvent-dependent chirality inversion of the CPL in dilute solution. The CPL spectra in CHCl$_3$ and 1,1,1-TCE were almost perfect mirror images of each other and the observed maxima for the $|g_{lum}|$ values were comparable to other non-switchable CPL materials in solution. Further studies on the development of other fluorescent and chirality-switchable helical poly(quinoxaline-2,3-diyl)s as a new class of CPL materials are currently in progress in our laboratory.

## Notes and references

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18 In our previous report,[15b] although $\Delta G_h$ of polymer **3** in CHCl$_3$ was determined as 0.10 kJ/mol by measurement of only 3 types of polymers (40, 100, and 200mers), the newly determined value 0.07 kJ/mol was more plausible because it was determined by the measurement of 7 types of polymer **3** (30 to 200mers).

**Chirality Switching of Circular Polarized Luminesence**

*M*-helical structure in chloroform

*P*-helical structure in 1,1,1-trichloroethane