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Aggregation-induced polarization (AIP) of derivatives of BINOL and BINAP†

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The relationship between optical rotations of small chiral molecules with water% in THF has been established. The typical aggregation co-solvent systems resulted in optical rotation amplification and adjustment, defined as aggregation-induced polarization (AIP). The AIP work can serve as a new tool to determine molecular aggregation, especially for those that cannot display aggregation-induced emission (AIE). Therefore, AIP and AIE are anticipated to complement each other. In addition, AIP can also serve as a new transmission tool providing adjusting right- or left-hand polarized lights of a series of individual wavelengths. Since chiral phosphine derivatives are among the most important ligands, this work would benefit research using chiral aggregates to control asymmetric synthesis and catalysts. Therefore, it will find many applications in chemical and materials sciences.

1 Introduction

For several decades, the research on chirality and chiral targets has been among the most active areas in science and technology communities.[1–7] Controlling chirality has resulted in high potency and selectivity for chiral pharmaceuticals and drugs,[8–11] challenging optical properties in radar, lasers, optical fibers, and wireless fiber telecommunications.[12–17] In measuring some of these properties, circular light polarization and optical rotations have been utilized to evaluate the performance of chiral molecules, in which optical fields rotate in a plane at a constant rate when the waves travel through their solutions.[18,19] The optical field is rotated toward the right- or left-hand direction during this measurement, called right- or left-circular polarization. It is noteworthy that circularly polarized luminescence (CPL) has become an active topic because of their potentials in display and optical storage devices, probes, and sensors.[15,16,20,21] CPL molecules directly generate polarized lights *via* emissions in a broad range of wavelengths in most cases. In contrast, the solutions containing chiral compounds are not able to result in polarized lights directly, which are originally emitted from metal or metal filament cycle lamps in a single wavelength of laser beams.[22,23]

In fact, aggregation-based CPL has attracted widespread attention since 2001, when Tang's group coined the concept of aggregation-induced emission (AIE) exhibiting strong fluorescence by aggregates states in solutions.[24–27] AIE was made possible by restricting intramolecular rotation and vibration to limit or avoid aggregation-caused quenching of luminophores. During the course of our ongoing project on chirality and chiral GAP (Group-Assistant-Purification) reagents, we found that a series of chiral compounds, including multi-layer 3D folding chiral compounds, can form chiral aggregates displaying strong AIE activities by gradually increasing water fractions (f_w) in THF–H_2O co-solvents. In turn, the observation of strong AIE fluorescence has proven the formation of various chiral aggregates of the aforementioned compounds. We wonder if the co-existence of various chiral aggregates in solutions can systematically lead to optical rotation enhancement or adjustment. These chiral aggregates cover not only AIE molecules but also those of aggregation-caused quenching (ACQ). To the best of our knowledge, the study of aggregation-induced effects on optical rotation has not been well documented. Very recently, our group investigated the relationship between the optical rotation of those chiral aggregates in multilayered chiral folding oligomers and polymers with increasing H_2O percentage in the co-solvent system, and we characterize this phenomenon as aggregation-induced polarization (AIP).[28] However, little is known regarding the existence of this phenomenon in small chiral molecules. Herein, we would like to report our preliminary results of this study.

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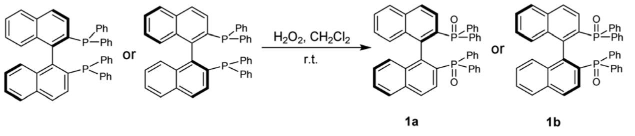
As mentioned above, the right- or left-polarized light beams *via* AIP transmission are originally emitted from metal or metal filament cycle lamps (external light sources). These polarized lights belong to laser beams of individual wavelengths. Therefore, AIP and AIE-based CPL would complement each other in studying chiral aggregates in solution and generating right- or left-polarized lights for future academic research and technological applications.

2 Results and discussion

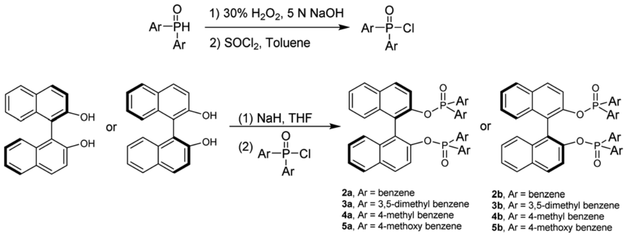
2.1 Synthesis

We started this project by taking advantage of GAP chemistry[29–33] and derivatives of BINAP and BINOLs, which are probably the most widely used chiral categories in asymmetric synthesis and catalysis. The selection of the simplest GAP group is based on two factors: (1) it is more likely to form chiral aggregates in solutions in THF and water; (2) they are readily available and concise to synthesize. (*S*)- or (*R*)-[1,1′-binaphthalene]-2,2′-diylbis(diphenylphosphine oxide), **1a** or **1b**, was thus synthesized simply by subjecting it to oxidation with hydrogen peroxide in DCM at room temperature overnight to give both yields of 94% (Scheme 1).[30]

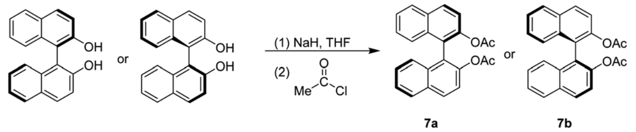
The two-step preparation of BINOL derivatives **2a–5b** was carried out in accordance with established methods and purified using GAP technology.[34] The first step involves the oxidation reaction of diphenylphosphine oxide with hydrogen peroxide in aqueous 5 N NaOH from 95 °C to 100 °C for 1 hour. The resulting crude product was directly subjected to the reaction with $SOCl_2$ in the presence of phosphonic acid in anhydrous toluene. The resulting solution was heated to 80 °C for 3 hours to give the protection crude product for work-up to give pure diphenylphosphinic chloride in a yield of 99%. The synthesis of (*S*)- or (*R*)-[1,1′-binaphthalene]-2,2′-diyl bis(diphenylphosphinate) was performed *via* deprotonation of BINOL with sodium hydride followed by dropwise addition of diphenylphosphinic chloride stirring at 0 °C for 15 minutes and then at room temperature overnight.[35] The GAP work-up simply by washing afforded pure derivatives of **2a** to **5b** in yields from 65% to 90% (Scheme 2).



Scheme 1 Oxidation of BINAP leading to **1a** and **1b**.



Scheme 2 Protection of BINOL leading to Derivatives of **2a** to **5b**.



Scheme 3 Protection of BINOL leading to **7a** and **7b**.

The generation of **7a** and **7b** is similar to that of **2a** and **2b** series by deprotonation of BINOL with sodium hydride, followed by adding acetyl chloride stirring at 0 °C for 15 minutes and then at room temperature overnight.[31,35] The work-up and flash chromatography purification gave pure **7a** and **7b** with both yields of 96% (Scheme 3).

2.2 AIE and AIP determination

To confirm the formation of chiral aggregates, we first determined aggregation-induced emission (AIE) of (*S*)-[1,1′-binaphthalene]-2,2′-diylbis(diphenylphosphine oxide) **1a** in THF and H_2O as co-solvents. As shown in Fig. 1a, this compound displayed an obvious AIE indicating an efficient formation of aggregates in THF/H_2O systems. The emission maxima of **1a** were gradually increased as the water fractions (f_w) were changed from 10% to 40%. There is a big jump in emission intensity from 0% to 10%. Relatively three large increments in emission intensity were observed when f_w was increased from 40% to 70% (Fig. 1a). Usually, the big jump could attribute to the suppression of molecular motion *via* intermolecular packing of the chiral axial molecule. As f_w continued to rise beyond 70%, the luminescence intensities were faintly weakened. A reasonable explanation was the motions between these individual molecules would decrease as the water fractions (f_w) became larger in dilute environments, resulting in loosely packed chiral aggregates.

The measurement of aggregation-induced polarization (AIP) was next planned on compound **1** under the above solvent systems. Rudolph polarimeter (Rudolph Research Analytical

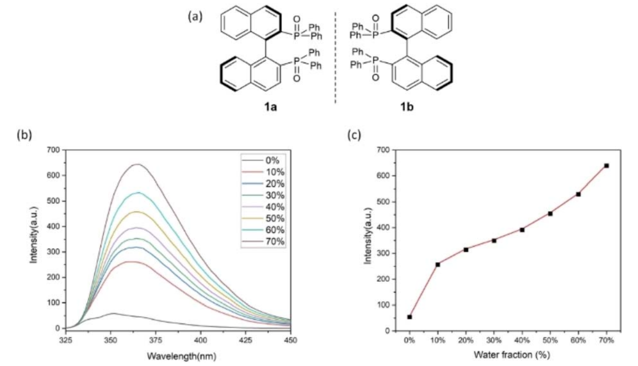


Fig. 1 (a) Structure of **1a** and **1b**. (b) PL spectra of **1a** in THF/water mixtures with different water fractions (f_w); $c = 0.1$ mM; $\lambda_{ex} = 326$ nm (c) Luminescence intensity of **1a** at 364 nm as a function of water fractions (f_w).

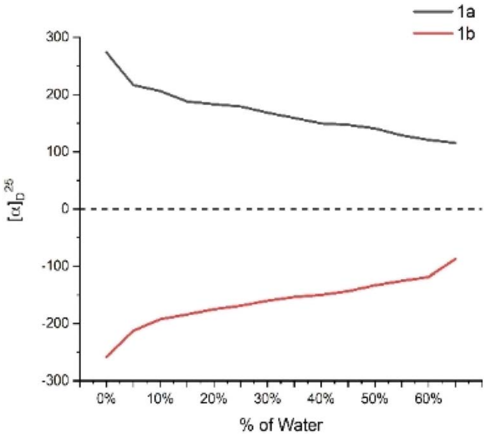


Fig. 2 Aggregation-induced polarization (AIP) of **1a** and **1b** in THF/water mixtures; $c = 4$ mg mL^{-1}.

APIV/2W) was utilized to acquire optical rotation data at room temperature with a sodium lamp as the light source (wavelength = 589 nm). Measurements were performed in a vessel of 2 mL with consistent concentration ($c = 4$ mg mL^{-1}) in THF and its co-solvents. The average data of three measurements for each sample was adopted in plotting the relationship curves. In this measurement, the water fraction (f_w) was set at the component of 5% (v/v) on *X*-horizontal coordinate corresponding to specific rotation on the *Y*-vertical ordinate. As revealed in Fig. 2, under the standard aggregation co-solvents of THF and water, we observed a consistent relationship between the specific optical rotation of chiral compound **1** and water fractions (f_w) by gradually increasing as water fractions (f_w) in co-solvents of THF–H_2O. When the fraction of water (f_w) exceeded 65%, the optical rotation data showed a certain degree of instability in this case, which would be attributed to the fact that the glass surface tension at the two ends of the vessel is enlarged depending on contents of chiral aggregates.

While the GAP function-anchored **1a** displayed strong aggregation-induced emission, other derivatives of chiral [1,1′-binaphthalene]-2,2′-diol (BINOL), **2a–5a**, did not show obvious AIE, which is a little surprising. However, these molecules exhibited consistent relationships of aggregation-induced polarization (AIP). As described in Fig. 3–8, each pair of their enantiomers showed a nearly symmetric relationship in AIP curves toward opposite directions of optical rotations.

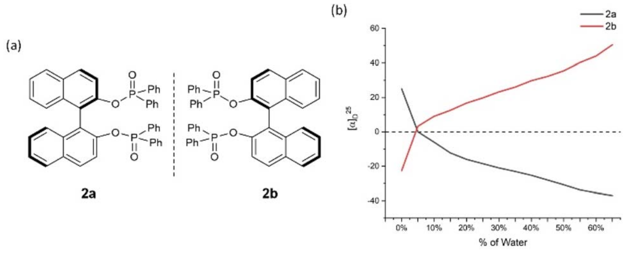


Fig. 3 **2a** and **2b** and their aggregation-induced polarization (AIP) in THF/water mixtures; $c = 4$ mg mL^{-1}.

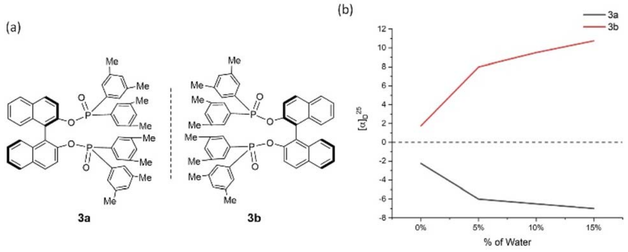


Fig. 4 **3a** and **3b** and their aggregation-induced polarization (AIP) in THF/water mixtures; $c = 4$ mg mL^{-1}.

In **2a**/**2b**, there are consistent enhancements of specific rotation from 25.0 to −37.0 and −22.5 to 50.5, respectively, when % water (f_w) was increased from 5% to 65% (Fig. 3). Specific rotation indicated an enhancement by a leap of over 20° between f_w of 0% and 5%. In the cases of **3a**/**3b**, a similar relationship to that of **2a**/**2b** was observed (Fig. 4). However, AIP only has stable optical rotation data within % water (f_w) range between 0% and 15%. The modest enhancement of aggregation-induced polarization (AIP) exists when % water (f_w) is increased from 5% and 15%. This is a larger AIP enhancement within % water range between 0% and 5%. Compared with the following cases, the special steric effect by 3,5-dimethyl groups on the GAP function would be attributed to the complicated situation associated with this narrow f_w range.

Cases of **4a**/**4b** and **5a**/**5b** showed relatively less congested GAP function than **3a**/**3b** and displayed AIP within a range of % water (f_w) from 0% to 45% and 0% to 40%, respectively (Fig. 5 and 6). A similar consistent relationship of aggregation-induced polarization was observed in these cases. However, both led to

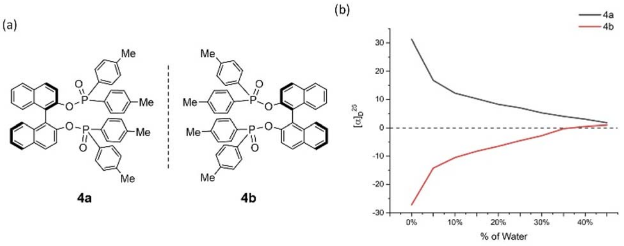


Fig. 5 **4a** and **4b** and their aggregation-induced polarization (AIP) in THF/water mixtures; $c = 4$ mg mL^{-1}.

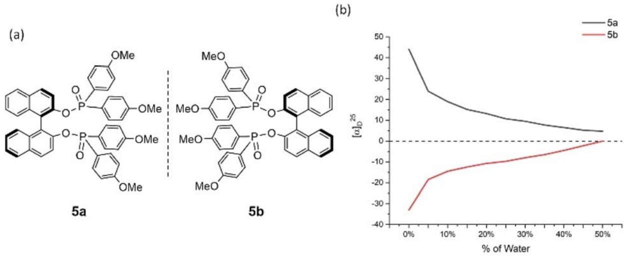


Fig. 6 **5a** and **5b** and their aggregation-induced polarization (AIP) in THF/water mixtures; $c = 4$ mg mL^{-1}.

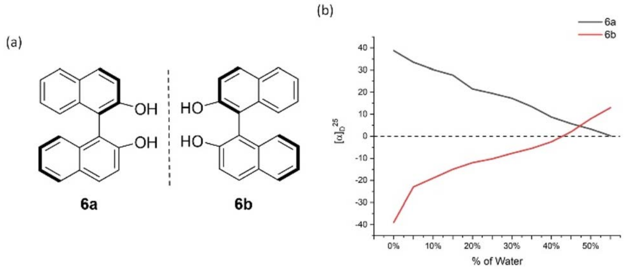


Fig. 7 **6a** and **6b** and their aggregation-induced polarization (AIP) in THF/water mixtures; $c = 4$ mg mL^{-1}.

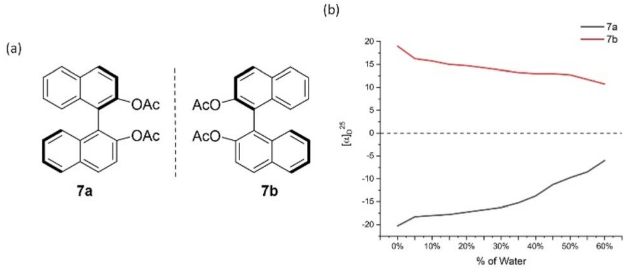


Fig. 8 **7a** and **7b** and their aggregation-induced polarization (AIP) in THF/water mixtures; $c = 4$ mg mL^{-1}.

specific rotation being adjusted decreasingly. This data is decreased to nearly zero when f_w for **4a** reaches 45% and for **5a** reaches 40%, respectively. There are relatively bigger optical rotation changes in both cases when f_w is increased from 0% to 5%.

After we successfully established the AIP-based GAP function of diarylphosphine oxides, the effect of concentrations on the AIP phenomenon was investigated. The AIP trends of diluted solutions remained nearly identical to those in 4 mg mL^{-1}. These results indicated that adjusting the concentration of chiral samples might not influence AIP. (Fig. S15†) On the other hand, we went back to check original (*S*)- and (*R*)-[1,1′-binaphthalene]-2,2′-diol (BINOL), **6a**/**6b**, and its derivative of [1,1′-binaphthalene]-2,2′-diyl diacetate, **7a**/**7b** (Fig. 7 and 8). Interestingly, both of these cases displayed the AIP relationship, albeit the AIP in the latter cases is weaker than its former counterparts. A consistent relationship of aggregation-induced polarization was observed, similar to the above two cases. Specific rotation is adjusted decreasingly for both cases. This data is even decreased to nearly zero when f_w for **6a** reaches 45% and for **7a** reaches 40%, respectively.

3 Conclusions

In conclusion, we have established the relationship between optical rotations of small chiral molecules with water% in THF. The typical aggregation co-solvent systems resulted in optical rotation amplification and adjustment, also known as aggregation-induced polarization (AIP). The AIP work can serve as a new tool to determine molecular aggregation, especially for those that cannot display aggregation-induced emission (AIE). Therefore, AIP and AIE are anticipated to complement each other. In addition, AIP can also serve as a new tool providing enhanced right- or left-hand polarized lights with individual wavelengths. Since chiral phosphines are among the most important ligands, this work would lead to new chiral aggregate-based asymmetric synthesis and catalysts. This work demonstrated that many synthetic reactions, especially asymmetric reactions, may be about behaviors of aggregates instead of individual molecules. A new standard of reporting-specific rotation would be explored to avoid the inconsistency of reporting this data in the literature. Therefore, it will find many applications in chemical and materials sciences. Extensive AIP scope on other solvents and chiral compounds will be investigated in our lab in due course.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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