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Volume 52 | Number 1 | 4 January 2016 | Pages 1–216

ChemComm

Chemical Communications
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ISSN 1359-7345

ROYAL SOCIETY OF CHEMISTRY

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COMMUNICATION

Strong Circularly Polarized Luminescence Induced from Chiral Supramolecular Assembly Helical Nanorods

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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The chiral supramolecular assemblies (BNS-BPP) can be self-assembled by electrostatic and π-π stacking interactions between chiral binaphthyl sulphonates (BNS) anion and the achiral bipyrene-based pyridinium (BPP) cation chromophore. BNS-BPP can exhibit strong CD and circularly polarized luminescence (CPL) signals, and the dissymmetry factor g_{lum} values can be up to 0.079.

Circularly polarized luminescence (CPL) is a unique chiroptical property of chiral luminescent systems (such as metal complexes,[1] small organic molecules,[2] polymers,[3] supramolecular assemblies[4]). As the emission analog of circular dichroism (CD) absorption spectrum, CPL emission has been regarded as one of the most important tools to investigate the excited-state features of chiral dyes.[5] Recently, there have been many reports on various CPL-emission materials for promising applications in information storage, photoelectric devices and chiroptical sensors.[6] Normally, the strategy of designing novel CPL materials is to introduce the chosen chiral moieties to the chromophores through covalent bonds or coordinate covalent bonds.[7] So far there have been few reports on CPL materials based on noncovalent interactions (such as electrostatic, hydrogen bonding and van der Waals interactions) *via* supramolecular self-assembly between the chiral sources and achiral chromophores.[8] Compared with common small organic molecules, chiral supramolecular assemblies can provide the enhanced CPL response signals as the molecular chirality can be effectively amplified through the assembly system.[9] Moreover, for multicomponent supramolecular assembly system, a series of CPL materials can be easily obtained by introducing different chiral sources and achiral chromophores into the supramolecular assembly system[8b,8e] Therefore, it is of great significance on developing novel CPL emission materials *via* chiral supramolecular assembly process.

Chiral supramolecular assemblies, which are the combinations of both nanoscale and chirality, have now played a vital role in the development of new materials for enantioselective sensing and separation,[10] chiral catalysis[11] and CPL emission[12]. Kawai's group reported that the chiral bichromophoric perylene bisimides (PBI) possessing cyclohexane as the chiral central core unit could exhibit CPL signals at both monomeric and assembled states, while the self-assembled structures showed more than an order of magnitude higher CPL dissymmetry factors compared with monomeric state of the molecule.[9a] Recently, our group also found that no CD or CPL signals of two perylene diimide (PDI) enantiomers incorporating a *D*/*L*-alanine moiety could be observed in $CHCl_3$ solution, but the *D*/*L*-PDI enantiomers could exhibit strong Cotton effects and CPL signals in the supramolecular self-assembly aggregations *via* the intermolecular π-π interaction upon the addition of the poor solvent MeOH to 99% fraction.[9b] However, chromophores like perylene bisimides suffered from aggregation-caused quenching (ACQ) phenomenon in aggregation state, which leads to the low fluorescence quantum yield of the supramolecular self-assemblies. In this paper, the chiral supramolecular assemblies can exhibit red fluorescent emission with good fluorescence quantum yield.

Optically active 1,1'-binaphthol (BINOL) and its derivatives have been widely studied as one of the most important chiral sources for designing CPL materials.[13] Akagi's group first reported blue CPL material of an interchain helically assembly between cationic π-conjugated polymers and anionic chiral binaphthyl derivatives through electrostatic and π-π interactions.[8d] Recently, Lu's group also discovered that the helical fiber assemblies between a TPE cationic and an anionic binaphthyl derivative could produce strong CPL response signals in cast films, and the g_{lum} values can reach as high as $+3.8 \times 10^{-2}$ and -4.2×10^{-2} for *S* and *R* configuration of binaphthyl derivatives in the assemblies, respectively.[14]

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†Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

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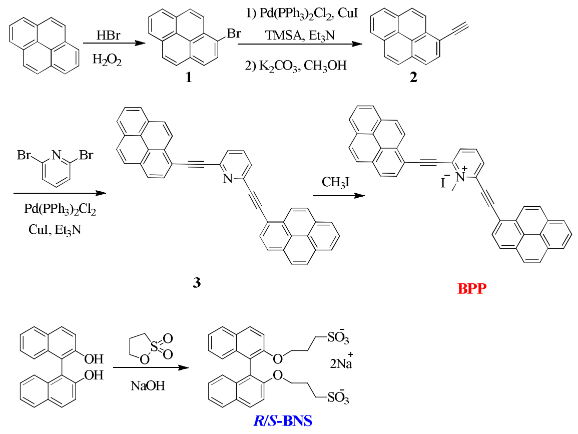
DOI: 10.1039/C7CC04363E

Herein, we designed the chiral supramolecular assemblies (BNS-BPP) between chiral binaphthyl sulphonates (BNS) and a bipyrene-based pyridinium (BPP) through electrostatic and π-π interactions. The aim of our design is to investigate the chiral transfer mechanism of BNS to chromophore BPP through electrostatic interaction. Then BPP can self-assemble *via* π-π stacking interactions under the chiral restriction of BNS. As a result, *R*/*S*-BNS-BPP can form *M*/*P*-helical nanorods and produce strong red-color CPL emission signals with +0.079/-0.070 of g_{lum} values.

The synthesis procedures of BPP and *R*/*S*-BNS are outlined in Scheme 1. Compound 1 and 2 were synthesized according to reported literatures.[15] Compound 3 was synthesized by Pd-catalyzed Sonogashira coupling reaction of 1-ethynylpyrene with 2, 6-dibromopyridine in 71% yield. BPP could be obtained from the quaternization of compound 3 with iodomethane in 86% yield. The detailed procedures and characterizations are described in the ESI. We have measured the FTIR spectra of BPP, *S*-BNS and *S*-BNS-BPP assemblies. As can be seen in Fig. S1, the peak at 2193 cm^{-1} can be assigned to the stretching vibration of triple bond in BPP. The two peaks at 1204 cm^{-1} and 1055 cm^{-1} can be ascribed to the asymmetric vibration and the symmetric vibration of the sulfonic group in BNS.[14] However, the characteristic peaks of sulfonic group shift to 1173 cm^{-1} and 1049 cm^{-1} in the chiral supramolecular assemblies *S*-BNS-BPP, which indicates the electrostatic interaction between BPP and BNS.



Scheme 1 The synthesis procedures of BPP and *R*/*S*-BNS.

The UV-*vis* absorption spectra of BNS, BPP and the chiral supramolecular assemblies (BNS-BPP) (molar ratio 1: 2, 1.0 × 10^{-5} mol/L for BPP) in MeOH-H_2O solution (50:50 *v*/*v*) are presented in Fig. 1. As shown in Fig. 1, BNS exhibits absorption bands at 228 nm and 275 nm, which can be assigned to the π-π* transition of the binaphthyl. The absorption band of BPP at 475 nm can be ascribed to the conjugated structure between pyrene and pyridine. But the assemblies BNS-BPP appears two additional absorption bands situated at 530 nm and 576 nm, which can be attributed to the formation of the chiral supramolecular assemblies BNS-BPP between BPP and BNS. In this paper the solvent effect experiments for UV-*vis* absorption spectra of BNS-BPP were carried out by changing water fraction of MeOH-H_2O solution system. As can be seen in Fig. 2, the absorption peaks at 475 nm slightly decreased as the water fraction (f_w) increased from 0 to 40%. Strangely, the absorption peak of BNS-BPP at 576 nm can be observed only when f_w is exactly 50%. When f_w is above 50%, this absorption peak disappears, but there appears a broad absorption band around 500 nm. We can draw a conclusion that 50% water fraction is the most suitable ratio of MeOH-H_2O mixed solvents for the formation of the chiral supramolecular assemblies BNS-BPP. As is evident from the Job's plot at the 576 nm absorption peak of BNS-BPP in MeOH-H_2O (50:50 *v*/*v*) (Fig. S2), the optimum mixing ratio of BNS: BPP is found to be 1.0: 2.0, which consists with the charge numbers of the two monomers.

The CD spectra of BNS-BPP were also measured in MeOH-H_2O solution at 50% water fraction. *R*/*S*-BNS-BPP can show obvious mirror-image CD signals (Fig. 1). The weaker positive-negative Cotton effects at 225 and 240 nm can be regarded as the feature absorption signals of chiral binaphthyl moiety in the chiral supramolecular assemblies BNS-BPP(Fig. S4). Strong Cotton effect of CD signals at long wavelength region can be observed, and the absorption dissymmetry factors (g_{abs}) can reach as high as +4.2 × 10^{-2} for *R*-BNS-BPP at 577 nm and -4.1 × 10^{-2} for *S*-BNS-BPP at 576 nm, respectively, which can be regarded as the absorption bands of the chiral supramolecular assemblies and demonstrate that the chirality has been successfully transferred from the chiral BNS anionic moiety to the achiral BPP cationic chromophore by electrostatic interaction. We observed that the further addition of BNS can form more BNS-BPP assemblies and lead to the enhanced CD absorption signals until the molar ratio of BNS/BPP reaches 1.5 (Fig. S3). We also investigate the CD behaviors in MeOH-H_2O solution by changing different water fractions. As can be seen in Fig. S4-S6, the CD spectra of BNS-BPP can only exhibit the CD signals of BNS when water fraction is below 40%. Compared to the CD signals at 576 nm at f_w =50%, only weaker positive-negative bisignals at 480 nm and 530 nm can be observed at f_w =80%, which indicates that the chirality can be greatly amplified at the most suitable ratio of MeOH-H_2O mixed solvents through the orderly and regular arrangement of the chiral supramolecular assemblies BNS-BPP.

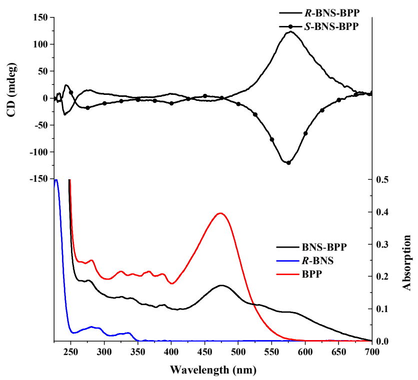


Fig. 1 UV-*vis* absorption spectra of BNS-BPP, *R*-BNS and BPP, CD spectra of BNS-BPP in MeOH-H_2O (50:50 *v*/*v*) solution (0.5 × 10^{-5} mol/L for BNS and 1.0 × 10^{-5} mol/L for BPP).

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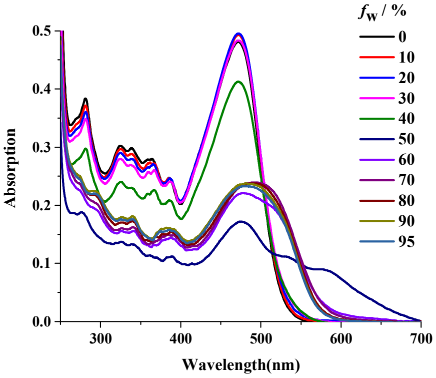

Fig. 2 UV-*vis* absorption spectra of BNS-BPP in MeOH-H$_2$O solution (0.5 × 10^{-5} mol/L for BNS and 1.0 × 10^{-5} mol/L for BPP).

The fluorescence and CPL spectra of BNS-BPP are presented in Fig. S7 and 3. BNS-BPP can exhibit red fluorescent emission at 605 nm in MeOH-H$_2$O (50:50 *v*/*v*) solution. There is almost no fluorescent emission at 605 nm for BPP in the absence of BNS (Fig. S7). Interestingly, the emission intensity of BPP at 605 nm gradually increases as the molar ratio increase of BNS until BNS: BPP is 2.0: 1.0, indicating the emission peak at 605 nm belongs to the chiral supramolecular assemblies BNS-BPP. The fluorescece quantum yield of BNS-BPP in MeOH-H$_2$O (molar ratio=1:2, f_w=50%) was measured to be 11.3%. Herein, CPL signals were performed by using JASCO CPL-300. As is evident from Fig. 3, the CPL response signals of BNS-BPP at 605 nm can exhibit obvious mirror-image positive (*R*-BNS-BPP) and negative (*S*-BNS-BPP) monosignals at f_w=50% of MeOH-H$_2$O solution. Meanwhile, we also found that almost no CPL signals can be detected at f_w=0%, 40%, 60% and 80% (Fig. S9 and S10), which further demonstrates that 50% water fraction is the most suitable ratio of MeOH-H$_2$O mixed solvents for the formation of the stable chiral supramolecular assemblies. According to the experimental determination of the CPL of *R*-BNS-BPP assembly with different molar ratio of BNS/BPP as shown in Fig. S8, the CPL signals can reach the maximum value at the 1:2 molar ratio of BNS/BPP although the molar ratio of BNS further increases, which also demonstrates that the chiral supramolecular assemblies can well consist with the charge numbers of BNS/BPP at the 1:2 molar ratio. Normally, the magnitude of circular polarization in the ground and excited states can be evaluated by dissymmetry factors g_{abs} and g_{lum}, respectively. The g_{abs} values of BNS-BPP are ±4.2 × 10^{-2} at about 576 nm, while the g_{lum} values of BNS-BPP are +7.9 × 10^{-2} (at 605 nm for *R* configuration) and -7.0 × 10^{-2} (at 605 nm for *S* configuration). The g_{abs} and g_{lum} values are on the order of 10^{-2} at the maximum absorption or emission wavelength, which can be attributed to the helical structures in the chiral supramolecular assemblies.[16]

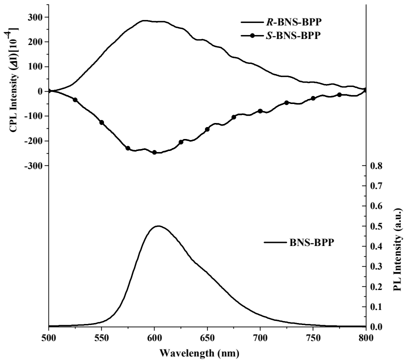

Fig. 3 Fluorescent and CPL spectra of BNS-BPP in MeOH-H$_2$O (50:50 *v*/*v*) solution (excitation: 467 nm, 0.5 × 10^{-5} mol/L for BNS and 1.0 × 10^{-5} mol/L for BPP).

The morphology study of the BNS-BPP assemblies was performed by scanning electron microscope (SEM). As is evident from Fig. 4, the morphologies of the chiral supramolecular assemblies are helical nanorods when the water fractions are 50%. The *R* and *S*-BNS in the assemblies can result in the left-handed (*M*-helicity) and right-handed (*P*-helicity) helical nanorods, which can well correspond to the positive and negative CPL signals of *R*-BNS-BPP and *S*-BNS-BPP. Meanwhile, we can discover that there are no helical nanorods when the water fractions are 0, 40%, 60% and 80% (Fig. S11), which is also coincident with the CD and CPL responses in different methanol-water mixtures. The self-assembly behaviors can be greatly influenced by the water fraction, which indicates that the chiral supramolecular assemblies can be formed by the co-effect of electrostatic interaction and π-π stack of pyrene.

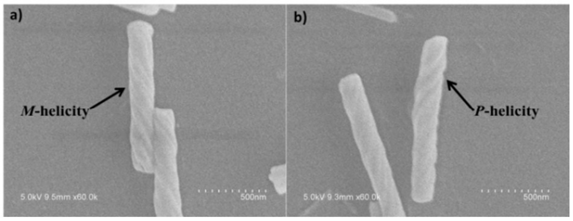

Fig. 4 SEM images of the chiral supramolecular assemblies of (a) *R*-BNS-BPP and (b) *S*-BNS-BPP obtained from drying the solutions of BNS-BPP in MeOH-H$_2$O (50:50 *v*/*v*). (0.5 × 10^{-5} mol/L for BNS and 1.0 × 10^{-5} mol/L for BPP)

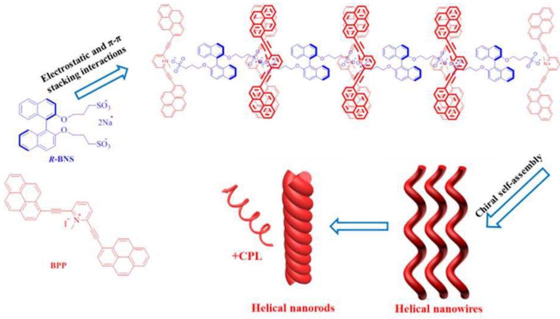

Fig. 5 Schematic illustration of hypothetical mechanism of the formation of *R*-BNS-BPP helical nanorods

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Herein we proposed the formation mechanism of the chiral supramolecular assemblies. As can be seen in Fig. 5, *R*-BNS first combines with BPP through electrostatic interaction and forms the left-handed helical nanowires *via* π-π stacking interaction. And then the left-handed helical nanowires can further bundle and form left-handed helical nanorods as shown in the SEM images (Fig. 4a).

In summary, the chiral binaphthyl sulphonates (BNS) and bipyrene-based pyridinium (BPP) were synthesized and then mixed together to generate the chiral supramolecular assemblies BNS-BPP. The chiral supramolecular assemblies can exhibit strong CD and CPL signals because of the chirality transfer from the chiral resources to achiral luminophores through the both effects of electrostatic and π-π interactions. The SEM images further support the optical properties of the chiral supramolecular assemblies. The dissymmetry factors g_{lum} can reach as high as 0.079, which is the most excellent CPL materials of the reported chiral organic molecules.

We would like to thank Prof. Lianhui Wang and Prof. Biqing Bao at IAM for their kind help with CPL measurements.This work was supported by the National Natural Science Foundation of China (21674046, 21474048 and 51673093)

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