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Plasmon resonance-enhanced circularly polarized luminescence of self-assembled *meso*-tetrakis-(4-sulfonatophenyl)porphyrin–surfactant complexes in interaction with Ag nanoparticles†

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The chiroptical properties of an anionic *meso*-tetrakis(4-sulfonatophenyl)porphyrin (TPPS) complexed with cationic surfactants were enhanced by interaction with silver nanoparticles (AgNPs) in acidic solution. Improvement in chiroptical properties was revealed by circular dichroism (CD) and circularly polarized luminescence (CPL), with $|g_{abs}|$ and $|g_{lum}|$ values reaching 0.05 and 0.001 at 303 K, respectively.

Materials that exhibit plasmon resonance enhancement are of particular interest given their unique optical properties, including their ability to exhibit electromagnetic field enhancement and to undergo strong exciton plasmon coupling.[1] Such properties allow for various potential applications in chemistry, biology, and optics, including use in ultrasensitive sensors and biological sensing and imaging.[1h] In particular, much attention has been paid to the optical and spectroscopic properties arising from the excitation of the surface electromagnetic modes of noble metal nanoparticles (NPs). The enhanced electromagnetic field induced by localized surface plasmon resonance (LSPR) can dramatically alter the properties of molecules near noble metal surfaces, resulting in many intriguing phenomena such as plasmonic circular dichroism (CD),[1b,2] surface-enhanced Raman scattering (SERS),[3] and surface-enhanced fluorescence (SEF).[1i,4] These surface-enhanced phenomena suggest that combining noble metal NPs with chiral molecules could aid in the development of novel molecular devices.

In this communication, we report a new example of plasmon-enhanced luminescence relating to circularly polarized luminescence (CPL), the differential emission ΔI ($I_L - I_R$) of right-circularly polarized light *versus* left-circularly polarized light by chiral molecular systems.[5] We focus specifically on the spectroscopic characteristics of well-ordered porphyrin assemblies because of their high photostability, strong Soret band absorption in the visible region, and high quantum yield resulting from the strong stacking interaction of their large delocalized π-electron system.[6] Among various porphyrins, the chiroptical properties of the water-soluble diprotonated 4-sulfonatophenyl *meso*-substituted porphyrin (TPPS) (Fig. 1)[7] have been studied extensively by several research groups due to the compound's unique chiral aggregation behaviour in acidic solution and the solid state.[8,9] As such, we have chosen this particular porphyrin because it is more cost-effective to make a CPL material with tunable chiroptical properties from achiral component(s) instead of a relatively costly chiral compound.

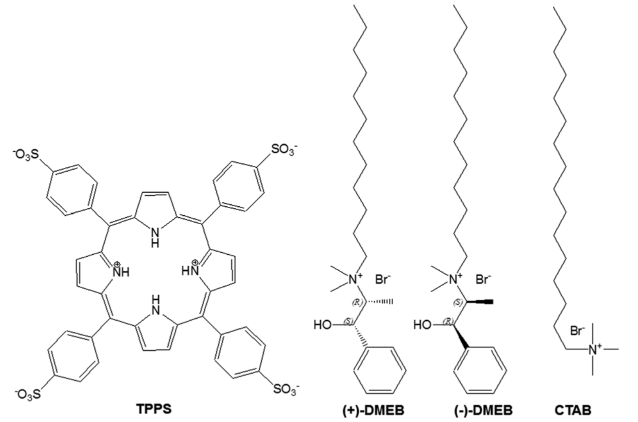

Fig. 1 The structure of TPPS and the surfactants (1*S*,2*R*)-*N*-dodecyl-*N*-methyl-ephedrinium bromide ((+)-DMEB), (1*R*,2*S*)-*N*-dodecyl-*N*-methyl-ephedrinium bromide ((−)-DMEB) and cetyltrimethylammonium bromide (CTAB).

Recently, we reported chiral control of a highly stable TPPS complex formed at the air–water interface that results by reacting the porphyrin with a cationic chiral surfactant.[10] Specific surfactants, such as chiral (1*S*,2*R*)- and (1*R*,2*S*)-*N*-dodecyl-*N*-methyl-ephedrinium bromide ((+)-DMEB and (−)-DMEB, respectively) as well as achiral cetyltrimethylammonium bromide (CTAB)[11]

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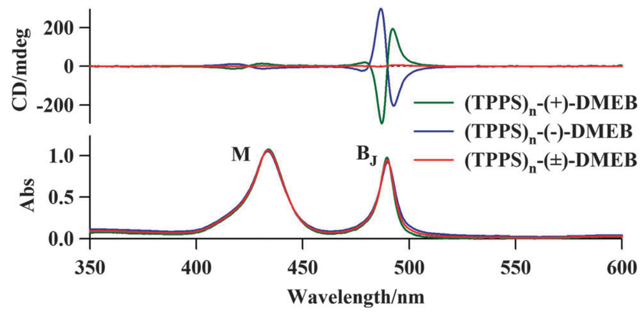

Fig. 2 Circular dichroism (CD) and electronic absorption spectra of $(TPPS)_n$ complexed with (+)-DMEB (green), (−)-DMEB (blue) and racemic DMEB (red) in acidic aqueous solution (pH = 2.3) 40 minutes after adding DMEB to a solution of $(TPPS)_n$; [TPPS] = 0.01 mM, [(+)-DMEB, (−)-DMEB or (±)-DMEB] = 0.01 mM, optical path length = 10 mm.

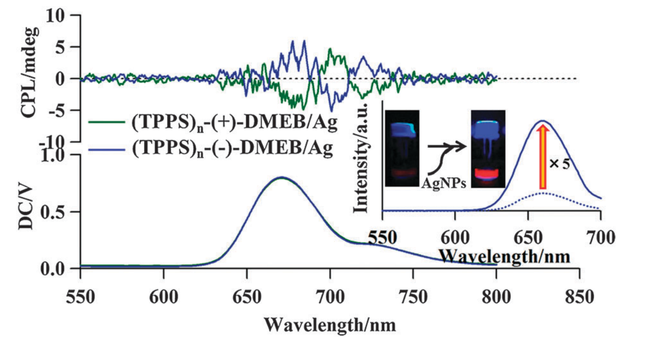

Fig. 3 CPL and fluorescence emission spectra of the composite $(TPPS)_n$–DMEB/AgNP solution ((+)-DMEB: green solid line, (−)-DMEB: blue solid line); [TPPS] = 0.01 mM, [(+)-DMEB, (−)-DMEB] = 0.01 mM, [AgNPs] = 0.05 mM, excitation wavelength (Ex = 430 nm), optical path length = 10 mm. The inset shows the fluorescence emission spectra before (dotted line) and after (solid line) adding AgNPs, and photographs show colour before (left) and after (right) adding AgNPs under a black light.

(as a control), were selected based on their properties as well-known chromophores that do not exhibit any electronic absorption in the visible range (B_J and Q-band), an important feature given the potential of surfactant molecules to limit absorption by the CPL-active complex (Fig. 1). In these experiments, cationic surfactants play a key role in the adsorption of citrate-capped NPs[12] to the helical TPPS assemblies, a process that is realized by substitution of citrate with a surfactant on the NP binding sites (see Fig. S2, ESI†). Furthermore, chiral surfactants allow for control of chirality of the aggregates as a whole.

The formation of self-assembled TPPS complexed with surfactants was tracked by FT-IR (Fig. S3, ESI†), UV-vis (Fig. S4, ESI†) and CD[13] spectroscopy. The CD signals obtained for TPPS complexed to (+)- and (−)-DMEB ($(TPPS)_n$–DMEB), respectively, were mirror images of each other (Fig. 2), while complexation with achiral CTAB showed no circular absorption, as per expectations. Control experiments using racemic DMEB showed no CD activity in the B_J band (Fig. 2). Meanwhile, kinetic data at λ_{max} (488 nm) fit well with theoretical equations for a first-order process, allowing determination of the pseudo-first-order rate constant K_{obs} (see Fig. S5, ESI†). The K_{obs} value was calculated to be 0.0147 min^{-1} for [TPPS] = 0.09 mM and [DMEB] = 0.09 mM, indicating that supramolecular chirogenesis proceeds slowly upon the addition of chiral DMEB. Additionally, the maximum value of artifact-free[13c] $|g_{abs}|$ was found to be 0.006 at 303 K, 40 min following the addition of DMEB to the solution (Fig. S6, ESI†). The amplification of the $|g_{abs}|$ ($4R/D$; $R = \mathrm{Im}[\mu_{ij}\cdot m_{ji}]$, $D = |\mu_{ij}|^2 + |m_{ji}|^2$) value was found to be directly proportional to the increase in rotational strength defined by the scalar product R because the total amount of self-assembled $(TPPS)_n$ remains unchanged during the chirogenesis process, implying that the dipole strength D is constant.

The surface plasmon resonance band for silver NPs (AgNPs), approximately 10 nm in size, is located at about 400 nm, demonstrating no overlap with the range of fluorescence for TPPS (Fig. S7, ESI†); as such, AgNPs were selected for complexation with $(TPPS)_n$–DMEB. These complexes ($(TPPS)_n$–DMEB/AgNPs)[14] were produced by adding citrate-capped AgNPs to a solution of fully formed $(TPPS)_n$–DMEB (see the experimental section in the ESI†). The formation of the target complexes was confirmed by direct observation using AFM (Fig. S8, ESI†), while binding of the AgNPs was also correlated with an increase in the $|g_{abs}|$ value (= $\Delta\varepsilon/\varepsilon$; 0.05 from 0.006 at 303 K) that was quantitatively consistent with the theoretical model.[1d] The size distribution of $(TPPS)_n$–DMEB hardly changed before and after the addition of AgNPs. Thus, it was speculated that the enhancement in the $|g_{abs}|$ value is mainly induced by the LSPR effect and is not due to an increase in the enantiomeric excess of the chiral aggregates, because the g-value is directly proportional to the scaling laws[15] for these nanoassemblies. Complex formation was also implied by the observed blue shift of the zero crossing and the Davydov splitting peak at the Soret bands (483 nm and 488 nm compared to 485 and 489 nm) from that observed for the unbound AgNPs (free $(TPPS)_n$–DMEB) (Fig. S6, ESI†).

The plasmon resonance-enhanced chiroptical properties of the formed complexes were then investigated by chiroptical spectroscopic methods. The fluorescence emission before and after the addition of AgNPs to the $(TPPS)_n$–DMEB solution (Fig. 3) indicates that emission is enhanced for the AgNP composite compared to the non-conjugated complex of AgNPs.[16] The composite exhibited two characteristic bands: the broad band at 670 nm is assigned to the monomeric form, while the low-energy shoulder emission band at 731 nm with moderate quantum yield ($\Phi = 0.1$) results from the J-bands of $(TPPS)_n$. Overall, AgNP binding resulted in an immediate five-fold increase in fluorescence intensities arising from the coupling of optical molecular dipoles with AgNPs (Fig. 3, inset).[17] This resulted in the observation of clear, detectable CPL signal intensities for $(TPPS)_n$–DMEB/AgNPs (Fig. 3) from concentrations of $(TPPS)_n$–DMEB that have a very low or undetectable level. For example, the maximum value of artifact-free $|g_{lum}|$ ($2\Delta I/I_L + I_R$) is 0.001 at 303 K, 40 minutes after addition of AgNPs to a $(TPPS)_n$–DMEB solution. As expected, the CPL curve of $(TPPS)_n$–(−)-DMEB/AgNPs was the mirror image of $(TPPS)_n$–(+)-DMEB/AgNPs. Overall, complexation appeared to modify the intrinsic R of the induced CPL bands of the TPPS–DMEB composite; this likely results from the interaction of the TPPS–DMEB composite with the silver surface and a concomitant change in conformational distribution. These results clearly demonstrate that signals observed for the enantiomeric composites are truly CPL[18,19] and are enhanced by the LSPR effect on the surface of AgNPs.

The enhancement contribution of the AgNPs indicates that this effect is related to the plasmon-induced electromagnetic enhancement responsible for other surface-enhanced optical phenomena such as SERS[3] and SEF.[1h] These changes in CPL intensities are the combined results of two effects: (1) CD enhancement and (2) quantum yield change due to increased excitation decay rates.[2] The quantum theory of the CPL effect of a single molecule provides us with the general equation $\mathrm{CPL_{mol}} = \mathrm{Im}[\mu_{ij}\cdot m_{ji}]$.[5] Here, we show that in the presence of a NP, this equation takes the form $\mathrm{CPL_{mol\text{-}NP}} = \mathrm{Im}[(\hat{P}\cdot\mu_{ij})\, m_{ji}]/(\omega_0 - \omega)^2 + F(\mu_{ij}, m_{ji})/(\omega_0 - \omega)$, where $\hat{P}$, $F(\mu_{ij}, m_{ji})$, ω_0 and ω are the electric-field enhancement matrix, the geometry of the complex, the frequency of the absorption band of a molecule, and the incident light frequency, respectively.[1b,d] As the factor $\hat{P}$ in the first term of the equation affects the angle between the vectors $\hat{P}\cdot\mu_{ij}$ and m_{ji}, any change in this value results in the CPL signal being altered.[20] In other words, this mechanism may create an enhanced chiral-field by the interaction of a chiral molecule with NPs.

Overall, we have demonstrated a new example of plasmon resonance-enhanced CPL of the $(\mathrm{TPPS})_n$–DMEB complex in interaction with AgNPs. The interaction of AgNPs with $(\mathrm{TPPS})_n$ through the surfactant DMEB resulted in the enhancement of the CD and CPL signals (enhanced $\Delta\varepsilon$ and ΔI) when compared with the pure $(\mathrm{TPPS})_n$–DMEB complex, a phenomenon which can be explained by the plasmon-induced resonant chiral-field enhancement arising from the coupling of optical molecular dipoles with AgNPs. This excitation of AgNP surface plasmons resulted in $|g_{\mathrm{abs}}|$ and $|g_{\mathrm{lum}}|$ values that were several times greater than in the unbound AgNPs. These results suggest a significant interaction between excitons and surface plasmons (exciton–plasmon coupling), with the potential for tuning the chiroptical properties of organic–NP complexes. Such control of chiral assemblies, consisting of achiral fluorescent compounds, through LSPR may ultimately result in high performance CPL materials.

Many organic compounds that exhibit CPL cannot effectively maintain both Φ and $|g_{\mathrm{lum}}|$ because of the nature of circularly polarized fluorophores (CPF).[5] Typically, efficient CPFs do not exhibit sufficient $|g_{\mathrm{lum}}|$, while those that do are not efficient. Optimization of the CPF Φ-$|g_{\mathrm{lum}}|$ trade-off is therefore a key consideration for the realization of desirable CPFs, with this LSPR-enhanced CPL being the first approach to achieve this goal. This was possible because this technique brings the values of both $\Delta\varepsilon$ and ΔI up to detectable levels, forcing both relatively high $|g_{\mathrm{lum}}|$ (order 10^{-3}) and Φ values.[21] We plan to further investigate the detailed mechanism of protean plasmon resonance-enhanced CD and CPL for $(\mathrm{TPPS})_n$–DMEB/AgNP complexes. Such investigations include tuning of chiroptical properties through changing the size and species of the NP cores, the spectral overlap between the J-band and the plasmon band, the stoichiometric ratio of TPPS and the NPs, and the distance between the fluorophore and the surface of the NPs.

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17 The enhancement of the CD and CPL signals induced by the LSPR effect was also observed upon interaction with other gold nanoparticles (data were not provided).

18 The signals could be obtained only by the Stokes–Mueller matrix analysis for true CPL signals because of the varying heights (∼20 nm) and widths (∼hundreds nm) of the optically anisotropic rod-like (TPPS)n aggregates.

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