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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 chirpoptical properties of anionic meso-tetrakis(4-sulfonatophenyl)porphyrin (TPPS) complexed with cationic surfactants were enhanced by interaction with silver nanoparticles (AgNPs) in acidic solution. Improvement in chirpoptical properties was revealed by circular dichroism (CD) and circularly polarized luminescence (CPL), with \(|g^{abs}|\) and \(|g^{num}|\) 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. Such properties allow for various potential applications in chemistry, biology, and optics, including use in ultrasensitive sensors and biological sensing and imaging.

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), surface-enhanced Raman scattering (SERS), and surface-enhanced fluorescence (SEF). 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 \(\Delta I (I_L - I_R)\) of right-circularly polarized light versus left-circularly polarized light by chiral molecular systems. 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 \(\pi\)-electron system.

Among various porphyrins, the chirpoptical properties of the water-soluble diprotinated 4-sulfonatophenyl meso-substituted porphyrin (TPPS) (Fig. 1) have been studied extensively by several research groups due to the compound’s unique chiral aggregation behaviour in acidic solution and solid state. As such, we have chosen this particular porphyrin because it is more cost-effective to make a CPL material with tunable chirpoptical properties from achiral component(s) instead of a relatively costly chiral compound.

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. Specific surfactants, such as chiral \((1S, 2R)\)- and \((1R, 2S)\)-Dodecyl-N-methyl-ephedrinium bromide \((\dagger)\)-DMEB and \((\ddagger)\)-DMEB, respectively) as well as achiral cetyltrimethylammonium bromide (CTAB) \((\ddagger)\) (as a control) were selected based on their properties as well-known chromophores that do not exhibit any electronic absorption in the visible range \((\pi, 1\text{-band})\), 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 to the helical TPPS assemblies, a process that is realized by substitution of citrate with surfactant on the NP binding sites (See Fig. S2). Furthermore, chiral surfactants allow for control of chirality of the aggregates as a whole.

![Fig. 1](image-url)

The formation of self-assembled TPPS complexed with surfactant was tracked by FT-IR (Fig. S3), UV-vis (Fig. S4) and CD spectroscopy. The CD signals obtained for TPPS complexed to \((\dagger)\)- and \((\ddagger)\)-DMEB ((TPPS), \((\dagger)\)-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 B1 band (Fig. 2). Meanwhile, kinetic data at \(\lambda_{max} (488\text{ nm})\) fits well with theoretical equations for a first-order process, allowing determination of the pseudo-first-order rate constant \(K_{obs}\) (see Fig. S5). The \(K_{obs}\) was calculated to be 0.0147 min\(^{-1}\) for [TPPS] = 0.09 mM, [DMEB] = 0.09 mM, indicating that supramolecular chirogenesis proceeds slowly upon the addition of chiral DMEB. Additionally, the maximum value of artifact-free \(|g_{abs}|\) was found to be 0.006 at 303 K, 40 min following the addition of DMEB to the solution (Fig. S6). The amplification of the \(|g_{abs}| (4R/D)\) \(R = \text{Im}(|\mu_{ij}|^2)\), \(D = |\mu_{ij}|^2\)
Because the total amount of demonstration no overlap with the range of fluoresce size, is located at about 40 nm, before and after the addition of AgNPs to the (TPPS) model. The formation of the target (Fig. 3) indicates that emission is enhanced for the AgNPs (see experimental section in SI). The formation of the target coupling of optical molecular dipoles with AgNPs. (Fig. 3 inset).

The broad band at 670 nm is assigned to the monomeric form, unbound AgNPs (free (TPPS)EDMEB) (Fig. S6). These complexes ((TPPS)EDMEB/AgNPs) were produced by adding citrate-capped AgNPs to a solution of fully formed (TPPS)EDMEB, which results from the interaction of the TPPSEDMEB composite and are enhanced by the LSPR effect on the surface of AgNPs. 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). This resulted in the observation of clear, detectable CPL signal intensities for (TPPS)EDMEB/AgNPs (Fig. 3) from concentrations of (TPPS)EDMEB/AgNPs that had a very low or undetectable level. For example, the maximum value of artifact-free $|g_{\text{lum}}|$ (2|ΔI/|I_0+|I_k|) is 0.001 at 303 K, 40 minutes after addition of AgNPs to a (TPPS)EDMEB solution. As expected, the CPL curve of (TPPS)EDMEB/AgNPs was the mirror image of (TPPS)EDMEB/AgNPs. Overall, complexation appeared to modify the intrinsic R of the induced CPL bands of the TPPS-EDMEB composite; this likely results from the interaction of the TPPS-EDMEB composite with the silver surface and a concomitant change in conformational distribution. These results clearly demonstrate that signals observed in the enantiomeric composites are truly CPL 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 the other surface-enhanced optical phenomena such as SERS and SEF. 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. The quantum theory of the CPL effect of a single molecule provides us with the general equation $\text{CPL}_{\text{mol}} = \text{Im}[\mu_{ij} m_{ij}]$. Here, we show that in the presence of a NP, this equation takes the form $\text{CPL}_{\text{mol-NP}} = \text{Im}[(P_{ji})_{ij} m_{ij}] (\omega_0 - \omega)^2 + F(m_{ij}) (\omega_0 - \omega)$, where $P$, $F$, $m_{ij}$, and $\omega$ 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. As the factor $P$ in the first term of the equation affects the angle between the vectors $P_{ji}$ and $m_{ij}$, any change in that value results in the CPL signal becoming altered. In other words, this mechanism may create an enhanced chiral-field by the interaction of a chiral molecule with NPs.
result in high performance CPL materials. Many organic compounds that exhibit CPL cannot effectively maintain both \(\Phi\) and \(I_{\text{em}}\) because of the nature of circularly polarized fluorophores (CPF). Typically, efficient CPFs do not exhibit sufficient \(I_{\text{em}}\) values, while those that do are not efficient. Optimization of the CPF \(\Phi-I_{\text{em}}\) 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 \(\Delta\gamma\) up to detectable levels, forcing both relatively high \(I_{\text{em}}\) (order 10\(^5\)) and \(\Phi\) values.

We plan to further investigate the detailed mechanism of protein plasmon resonance-enhanced CD and CPL for (TPPS)\(_2\)-DMEB/AgNPs 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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### Notes and references

13. (+)-DMEB (Fig. 1) was prepared from (1S,2R)-norephedrine according to a previously reported method (see Experimental Section and Fig. S1 in ESf). CTAB and (-)-DMEB were purchased from Tokyo Kasei Co. Ltd., and used without any further treatment.
17. NP binding was confirmed by Fourier Transform Infrared Spectroscopy (FT-IR), as shown in Supporting Information Fig. S3. The FT-IR spectrum showed the presence of IR stretching frequencies for the \(\nu\text{C}=\text{O}\) (3000-2800 cm\(^{-1}\)) region and \(\nu\text{S}=\text{O}\) (1080-1000 cm\(^{-1}\)) region bands, which were shifted from those observed in the unbound NPs and (TPPS)\(_2\)-DMEB-AgNPs, respectively.
19. The effect of the distance between the AgNPs surface and fluorophore on the CD and CPL enhancements was investigated using surfactants having different alkyl chain lengths, ranging from 6 to 12 carbon atoms; however, we did not observe any effect on the SPR enhancement for this range of alkyl chain lengths (data was not shown).
20. The enhancement of the CD and CPL signals induced by the LSPR effect was also observed upon interaction with other gold nanoparticles. (data was not shown)
21. The effect of the distance between the AgNPs surface and fluorophore on the CD and CPL enhancements was investigated using surfactants having different alkyl chain lengths, ranging from 6 to 12 carbon atoms; however, we did not observe any effect on the SPR enhancement for this range of alkyl chain lengths (data was not shown).
22. The effect of the distance between the AgNPs surface and fluorophore on the CD and CPL enhancements was investigated using surfactants having different alkyl chain lengths, ranging from 6 to 12 carbon atoms; however, we did not observe any effect on the SPR enhancement for this range of alkyl chain lengths (data was not shown).
23. The magnitude of \(g\) is related to the amount of magnetic dipole character in the transition: high \(g\) values (order 10\(^{-3}\)) are expected for \(m\)-allowed and \(\mu\)-forbidden transitions, respectively, of course, that the chromophore is contained in a molecular structure that is sufficiently disymmetric. For \(m\)-forbidden and \(\mu\)-allowed transitions, small values (order \(10^{-3}\)) are predicted.
25. The signals could be obtained only by the Stokes-Mueller matrix analysis for true CPL signals because of the varying heights (\(\sim 20\) nm) and widths (\(\sim\) hundreds nm) of the optically anisotropic rod-like (TPPS)\(_2\) aggregates.
27. The magnitude of \(g\) is related to the amount of magnetic dipole character in the transition: high \(g\) values (order \(10^{-3}\)) are expected for \(m\)-allowed and \(\mu\)-forbidden transitions, respectively, of course, that the chromophore is contained in a molecular structure which is sufficiently disymmetric. For \(m\)-forbidden and \(\mu\)-allowed transitions, small values (order \(10^{-3}\)) are predicted.