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 anionic meso-tetrakis(4-sulfonatophenyl)porphyrin (TPPS) complexed with cationic surfactants were enhanced by interaction with silver nanoparticles (AgNPs) in acidic solution. Improvement in
10 **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,
15 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].
20 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
25 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
30 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
35 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
40 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
45 to the compound's unique chiral aggregation behaviour in acidic solution and 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
50 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.[10] Specific surfactants, such as chiral (1S,2R)- and (1R,2S)-N-

55 Dodecyl-N-methyl-ephedrinium bromide ((+)-DMEB and (-)-DMEB, respectively) as well as achiral cetyltrimethylammonium bromide (CTAB)[11] (as a control) were selected based on their properties as well-known chromophores that do not exhibit any electronic absorption in
60 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
65 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.
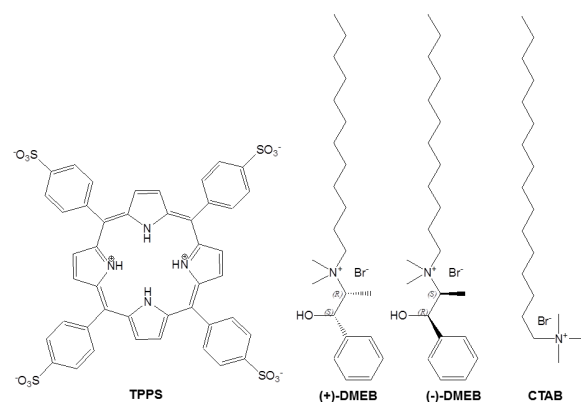

Fig. 1 The structure of TPPS and the surfactants (1S,2R)-N-Dodecyl-N-methyl-ephedrinium bromide ((+)-DMEB), (1R,2S)-N-
70 Dodecyl-N-methyl-ephedrinium bromide ((-)-DMEB) and cetyltrimethyl-ammonium bromide (CTAB).

The formation of self-assembled TPPS complexed with surfactant was tracked by FT-IR (Fig. S3), UV-vis (Fig. S4)
75 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
80 racemic DMEB showed no CD activity in the B_J band (Fig. 2). Meanwhile, kinetic data at λ_{max} (488 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
85 [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[13c] $|g_{abs}|$ was found to be 0.006 at 303 K, 40 min following the addition of DMEB to the solution (Fig. S6). The
90 amplification of the $|g_{abs}|$ ($4R/D$; $R = \text{Im}[\mu_{ij} \cdot m_{ji}]$, $D = |\mu_{ij}|^2 +$

$|m_{ji}|^2$) 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 the dipole strength D is constant.

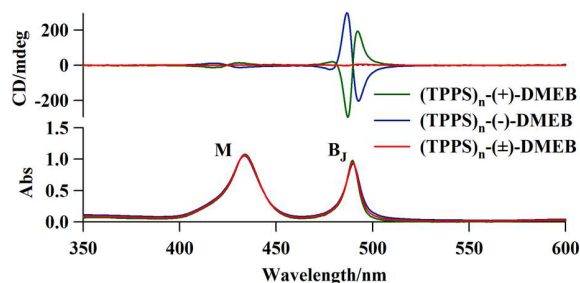**Fig. 2** Circular dichroism (CD) and electronic absorption spectra of $(TPPS)_n$ complexed with (+)-DMEB (green)**,** (-)-DMEB (blue) and racemic DMEB (red) in acidic aqueous solution (pH =2.3) 40 minutes after adding DMEB to a solution of $(TPPS)_n$; [TPPS] = 0.01 mM, [(+)-DMEB**,** (-)-DMEB or (±)-DMEB]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

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); 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 experimental section in SI). The formation of the target complexes was confirmed by direct observation using AFM (Fig S8), while binding of the AgNPs was also correlated to 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 in the unbound AgNPs (free $(TPPS)_n$-DMEB) (Fig. S6).

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 AgNPs 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 had 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 in 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 the 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 $CPL_{mol} = Im[\mu_{ij} \cdot m_{ji}]$.[5] Here, we show that in the presence of a NP, this equation takes the form $CPL_{mol\text{-}NP} = Im[(P \cdot \mu_{ij}) \cdot m_{ji}]/(\omega_0-\omega)^2 + F(\mu_{ij}, m_{ji})/(\omega_0-\omega)$, where 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,1d] As the factor P in the first term of the equation affects the angle between the vectors $P \cdot \mu_{ij}$ and m_{ji}, any change in that value results in the CPL signal becoming altered.[20] In other words, this mechanism may create an enhanced chiral-field by the interaction of a chiral molecule with NPs.
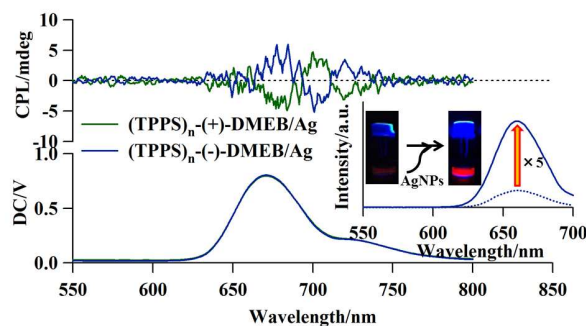

Fig. 3. CPL and fluorescence emission spectra of the composite $(TPPS)_n$-DMEB/AgNPs solution ((+)-DMEB: green solid line, (-)-DMEB: blue solid line); [TPPS] = 0.01 mM, [(+)-DMEB**,** (-)-DMEB] = 0.01 mM, [AgNPs] = 0.05 mM, excitation wavelength (Ex = 430 nm), optical path length = 10 mm. The inset shows 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.

Overall, we have demonstrated a new example of plasmon resonance-enhanced CPL of the $(TPPS)_n$-DMEB complex in interaction with AgNPs. The interaction of AgNPs with $(TPPS)_n$ through the surfactant DMEB resulted in the enhancement of the CD and CPL signals (enhanced $\Delta\varepsilon$ and ΔI) when compared with pure $(TPPS)_n$-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 $|g_{abs}|$ and $|g_{lum}|$ 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 $|g_{lum}|$ because of the nature of circularly polarized fluorophores (CPF).[5] Typically, efficient CPFs do not exhibit sufficient $|g_{lum}|$, while those that do are not efficient. Optimization of the CPF Φ-$|g_{lum}|$ 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 $|g_{lum}|$ (order 10^{-3}) and Φ values.[21] We plan to further investigate the detailed mechanism of protean plasmon resonance-enhanced CD and CPL for $(TPPS)_n$-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.

Notes and references

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†Electronic Supplementary Information (ESI) available: Experimental Section, Figs. S1-S8. See DOI: 10.1039/b000000x/

1. a) M. Schaferling, X. Yin, N. Engheta and H. Giessen, *ACS Photonics*, 2014, DOI: 10.1021/ph5000743; b) Z. Li, Z. Zhu, W. Liu, Y. Zhou, B. H. Han, Y. Gao and Z. Tang, *J. Am. Chem. Soc.*, 2012, **134**, 3322; c) J. M. Slocik, A. O. Govorov and R. R. Naik, *Nano Lett.*, 2011, **11**, 701; d) A. O. Govorov, *J. Phys. Chem. B*, 2011, **115**, 7914; e) A. O. Govorov, Z. Fan, P. Hernandez, J. M. Slocik and R. R. Naik, *Nano Lett.*, 2010, **10**, 1374; f) A. Yoshida and N. Kometani, *J. Phys. Chem. C.* 2010, **114**, 2867; g) T. Sato, A. Omura and Y. kobayashi, *Bull. Chem. Soc. Jpn.*, 2010, **83**, 1052; h) Jeffrey N. Anker, W. Paige Hall, Olga Lyandres, Nilam C. Shah, Jing Zhao and Richard P. Van Duyne, *Nature Materials*, 2008, **7**, 442; i) Li-Q. Chu, R. Forch and W. Knoll, *Angew. Chem.*, 2007, **119**, 5032.

2. a) B. M. Maoz, R. van der Weegen, Z. Fan, A. O. Govorov, G. Ellestad, N. Berova, E. W. Meijer and G. Markovich, *J. Am. Chem. Soc.* 2012, **134**, 717807; b) A. O. Govorov, Y. K. Gun'ko, J. M. Slocik, V. A. Gerard, Z. Fana and R. R. Naik, *J. Mater. Chem.*, 2011, **21**, 16806; c) I. Lieberman, G. Shemer, T. Fried, E. M. Kosower and G. Markovch, *Angew. Chem. Int. Ed.*, 2008, **47**, 4855.

3. a) C. E. Talley, J. B. Jackson, C. Oubre, N. K. Grady, C. W. Hollars, S. M. Lane, T. R. Huser, P. Nordlander and N. J. Halas, *Nano, Lett.*, 2005, **5**, 1569; b) A. M. Michaels, J. Jiang and L. Brus, *J. Phys. Chem. B.*, 2000, 104, 11965; c) J. Gersten1 and A. Nitzan, *J. Chem. Phys.* 1980, **73**, 3023.

4. a) A. Kinkhabwala, Z. F. Yu, S. H. Fan, Y. Avlasevich, K. Mullen and W. E. Moerner, *Nat. Photonics* 2009, **3**, 654; b) O. L. Muskens, V. Giannini, J. A. Sanchez-Gil and J. G. Rivas, *Nano Lett.*, 2007, **7**, 2871.

5. H. P. J. M. Dekkers, Circularly polarized luminescence. a probe for chirality in the excited state, in: N. Berova, K. Nakanishi, R.W. Woody (Eds.), Circular Dichroism: Principle and Application, Wiley-VCH, 2000.

6. O. Ohono, Y. Kaizu and H. Kobayashi, *J. Chem. Phys.*, 1993, **99**, 4128.

7. The driving force for the formation of aggregates is the intermolecular interaction between the positively charged centre of a diprotonated porphyrin ring and the negatively charged peripheral sulfate groups of another TPPS molecule.

8. a) S. Jiang, L. Zhang and M. Liu, *Chem. Commun.*, 2009, 6252; b) L. Posaria, A. D'Urso, A. Mammana and R. Purrello, *Chirality*, 2008, **20**, 411; c) H. Onouchi, T. Miyagawa, K. Morino and E. Yashima, *Angew. Chem. Int. Ed.*, 2006, **45**, 2381; d) C. Escudero, J. Crusats, I. D-Perez, Z. El-Hacemi and J. M. Ribo *Angew. Chem. Int. Ed.*, 2006, **45**, 8032; e) T. Yamaguchi, T. Kimura, H. Matsuda, andT. Aida, *Angew. Chem. Int. Ed.* 2004, **43**, 6350; f) J. M. Ribo, J. Crusats, F. Sagues, J. Claret and R. Rubires, *Science*, 2001, **292**, 2063.

9. a) Z. El-Hachemi, O. Arteaga, A. Canillas, J. Crusats, C. Escudero, R. Kuroda, T. Harada, M. Rosa and J. M. Ribo, *J. Eur. Chem.*, 2008, **14**, 6438; b) V. V. Borovkov, T. Harada, G. A. Hembury, Y. Inoue and R. Kuroda, *Angewandte Chem. Int. Ed.*, 2003, **42**, 1746; c) V. V. Borovkov, T. Harada and Y. Inoue, R. Kuroda, *Angew. Chem. Int. Ed.* 2002, **41**, 1378.

10. T. Harada, H. Takahashi, K. Umemura, H. Moriyama, H. Yokota, R. Kawakami and K. Mishima, *Appl. Spectrosc.* 2014, in press.

11. (+)-DMEB (Fig. 1) was prepared from (1*S*,2*R*)-(+)-norephedrine according to a previously reported method (see Experimental Section and Fig. S1 in ESI†). CTAB and (-)-DMEB were purchased from Tokyo Kasei Co. Ltd., and used without any further treatment.

12. a) H. Wang, J. Kundu and N. J. Halas, *Angew. Chem. Int. Ed.* 2007, **46**, 9040; b) Z. M. Sui, X. Chen, L. Y. Wang, L. M. Xu, W. C. Zhuang, Y. C. Chai and C. J. Yang, *Physica E*, 2006, **33**, 308.

13. a) T. Harada and R. Kuroda, *Biopolymers*, 2011, **95**, 127; b) T. Harada, H. Hayakawa and R. Kuroda, *Rev. Sci. Instrum.*, 2008, **79**, 073103; c) R. Kuroda, T. Harada and Y. Shindo, *Rev. Sci. Instrum.*, 2001, **72**, 3802.

14. 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 vCH_2 (3000-2800 cm^{-1} region) and $vRSO_3H$ (1080-1000 cm^{-1} region) bands, which were shifted from those observed in the unbound NPs and $(TPPS)_n$-DMEB-AgNPs, respectively.

15. a) A. Romeo, M. A. Castriciano, I. Occhiuto, R. Zagami, R. F. Pasternack and L. M. Scolaro, *J. Am. Chem. Soc.*, 2014, **136**, 40; b) M. A. Castriciano, A. Romeo, G. De. Luca, V. Villari, L. M. Scolaro and N. Micali, *J. Am. Chem. Soc.*, 2011, **133**, 765.

16. 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).

17. 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)

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.

19. T. Harada, R. Kuroda and H. Moriyama, *Chem. Phys. Lett.*, 2012, **530**, 126.

20. The magnitude of g is related to the amount of magnetic dipole character in the transition: high g values (order 10^{-1}) are only expected for *m*-allowed and μ-forbidden transitions provided, of course, that the chromophore is contained in a molecular structure that is sufficiently dissymmetric. For *m*-forbidden and μ-allowed transitions, small values (order $<10^{-3}$) are predicted.

21. a) B. A. San Jose, S. Matsushita and K. Akagi, *J. Am. Chem. Soc.*, 2012, **134**, 19795; b) K. Watanabe, I. Osaka, S. Yorozuya and K. Akagi, *Chem. Mater.*, 2012, **24**, 1011; c) S. Abraham, S. Paul, G. Narayan, S. K. Prasad and N. D. S. Jayaraman, *Adv. Funct. Mater.*, 2005, **15**, 1579.