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Letter

# Optical Axial Chirality Enhancement and Transfer within Aromatic Micelles upon (Co-)encapsulation

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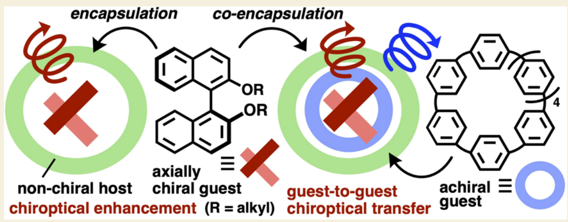
ABSTRACT: Axial chirality is the key physiochemical element, yet its chiroptical utilities have been largely limited to covalent synthesis and infinitely assembled systems so far. Here we report a new application of axially chiral binaphthyls for efficient, optical chirality enhancement and transfer upon noncovalent encapsulation by achiral aromatic micelles in water. The CD activities of dialkoxy binaphthyls are significantly enhanced (up to 7-fold) upon encapsulation by an anthracene-based aromatic micelle. Large emission enhancement (~4-fold) and efficient guest-to-guest, optical chirality transfer are achieved through coencapsulation of the binaphthyls with achiral cycloparaphenylenes, in a guest-within-guest fashion, by the micelle. The observed unusual properties are derived from the tight inclusion of the chiral guests into the macrocyclic guests, efficiently generated only in the aromatic cavity. Moderate CPL can be observed from the coencapsulated macrocycles within the ternary composites. Furthermore, more than ~4-fold enhanced guest-to-guest chiroptical transfer is demonstrated with a functionalized cycloparaphenylene through the present coencapsulation strategy.




KEYWORDS: *axial chirality transfer, binaphthyl compounds, coencapsulation, cycloparaphenylene, aromatic micelle*

Axial chirality, based on restricted rotation around a single bond, is typically found in biaryl compounds.[1] Unlike central and planar chiralities, the chiral properties largely depend on the dihedral angle between the aromatic panels. Among them, binaphthyl is one of the most useful, axially chiral components, e.g., for applications in enantioselective sensors, chiroptical materials, and asymmetric catalysis,[2] due to the high configurational stability, asymmetrical bulkiness, and synthetical accessibility. To further enhance and expand the characteristic chiroptical functions, the development of rational chirality transfer systems from axially chiral components to nonchiral dyes is much in demand at the molecular level. The majority of the studies have been performed with covalent linkages (Figure 1a), e.g., employing perylene bisimide and boron-dipyrromethene dyes,[3] as well as infinite molecular assemblies.[4] Whereas efficient, optical chirality transfer can be found by these methods, laborious syntheses or huge assemblies are usually required. Finite host−guest complexation is an alternative method, using chiral hosts and achiral dye guests.[5] Various cage-shaped hosts have been prepared so far, e.g., from metal hinges and organic ligands embedding axially chiral units (Figure 1b). However, efficient host-to-guest chirality transfer was seldom accomplished in the cavity, owing to weak or no host−guest interactions.[6] To advance the host−guest methodology, here we propose a new coencapsulation strategy by combining axially chiral compounds and achiral dyes with a non-chiral host (Figure 1c).

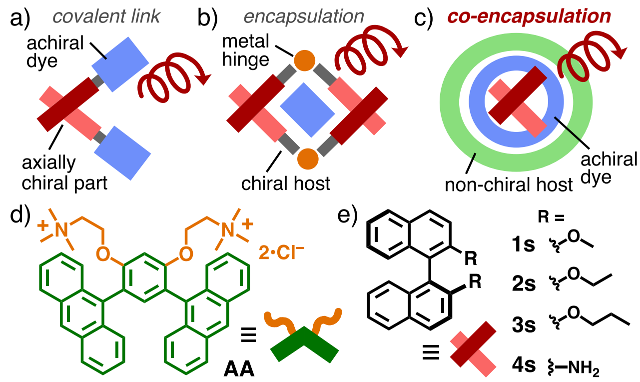



**Figure 1.** Schematic representation of optical axial chirality transfer systems: a) a covalent compound and noncovalent host−guest composites using b) a chiral host and c) a nonchiral host (this work). d) Bent aromatic amphiphile **AA** and e) (*S*)-binaphthyl derivatives **1**-**4s**.

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We herein report (i) the circular dichroism (CD) enhancement of binaphthyl derivatives (up to 6.9-fold) upon encapsulation by achiral aromatic micelles in water, (ii) the emission enhancement of cycloparaphenylene dyes in the micelle (up to 4.3-fold; $\Phi_F$ = 86%) upon coencapsulation with binaphthyls, (iii) efficient guest-to-guest, optical chirality transfer to the achiral macrocycles ($|g_{abs}|$ = up to 2.4 × $10^{-4}$), and (iv) the unusual observation of circularly polarized luminescence (CPL; $|g_{lum}|$ = up to 2.5 × $10^{-4}$) from the coencapsulated, achiral guests. (v) The same coencapsulation protocol also enables multifunctionalized cycloparaphenylene to be chiroptically active to a large extent (i.e., $|g_{abs}|$ = 1.4 × $10^{-3}$, $|g_{lum}|$ = 9.5 × $10^{-4}$). The present new host−guest strategy is expected to deepen and widen axial chirality-based optical chemistry.

Efficient coencapsulation of two kinds of molecules has been widely studied using both covalent/noncovalent tubular, cage-shaped, and capsular compounds.[7,8] Although various molecules in the range of small to large sizes could be simultaneously encapsulated by these hosts, the successful coencapsulation of axially chiral compounds with macrocyclic dyes has yet to be reported. Aromatic micelle $(\mathbf{AA})_n$ is an aqueous achiral capsule,[9] composed of bent aromatic amphiphiles **AA** (Figure 1d), featuring two anthracene panels and two ammonium groups. The discrete, adaptable polyaromatic cavity of $(\mathbf{AA})_n$ can accommodate various achiral aromatic molecules (e.g., organic dyes and metal-complexes) in water, through efficient hydrophilic effect as well as $\pi-\pi$ and CH-$\pi$ interactions.[10] To unveil the host ability toward axially chiral compounds, in this report, we for the first time employ (*S*)/(*R*)-binaphthyl derivatives **1**-**4**, bearing two methoxy, ethoxy, propoxy, and amino groups, respectively (Figure 1e). [9]Cycloparaphenylene[11] and its multimethoxy derivative[12] are selected as coencapsulated dyes, with a rigid and highly symmetrical, macrocyclic framework (1.2 nm in diameter) and high/moderate emission properties, for unusual guest-to-guest, optical chirality transfer in the aromatic cavity.[13,14]

Axially chiral compound **1s** ((*S*)-isomer, R = $OCH_3$) was efficiently encapsulated by aromatic micelle $(\mathbf{AA})_n$, superior to other micelles tested herein, in water through a grinding protocol (Figure 2a). A mixture of **AA** (1.0 $\mu$mol) and water-insoluble **1s** (2.0 $\mu$mol) was ground using a mortar and pestle for 1 min. Subsequently, water (1.0 mL) was added to the solid, and the resultant suspension was centrifuged (16000*g*, 10 min) and filtered (pore size: 200 nm) to yield a clear colorless solution containing host−guest composite $(\mathbf{AA})_n\cdot(\mathbf{1s})_m$ without free **1s**.[15,16] The manual grinding is essential to facilitate **AA**-**1s** interactions prior to adding water (Figure S17). The UV−visible spectrum of the aqueous solution showed broad absorption bands at 280−350 nm, attributed to bound $(\mathbf{1s})_m$, along with the anthracene-based vibronic bands (320−420 nm) of $(\mathbf{AA})_n$ (Figure 2b). The product structure, a spherical $(\mathbf{AA})_{27}\cdot(\mathbf{1s})_{18}$ assembly on average, was revealed by DLS, NMR-based host−guest ratio, and molecular modeling analyses. The DLS chart displayed a single peak at 4.0 nm (Figure 2c), as an average core diameter of the product, in water, unlike that of empty $(\mathbf{AA})_n$ ($d_{av.}$ = 1.5 nm). The $^1$H NMR-based integrals of the isolated product (via lyophilization) in $CD_3CN$ indicated its average **AA**:**1s** ratio being 3:2 (Figure S7b). The molecular modeling studies based on the DLS and NMR data suggested the formation of a large spherical particle, composed of an 18·**1s** core and a 27·**AA** shell, with a calculated core diameter of 4.0 nm (Figure 2d).

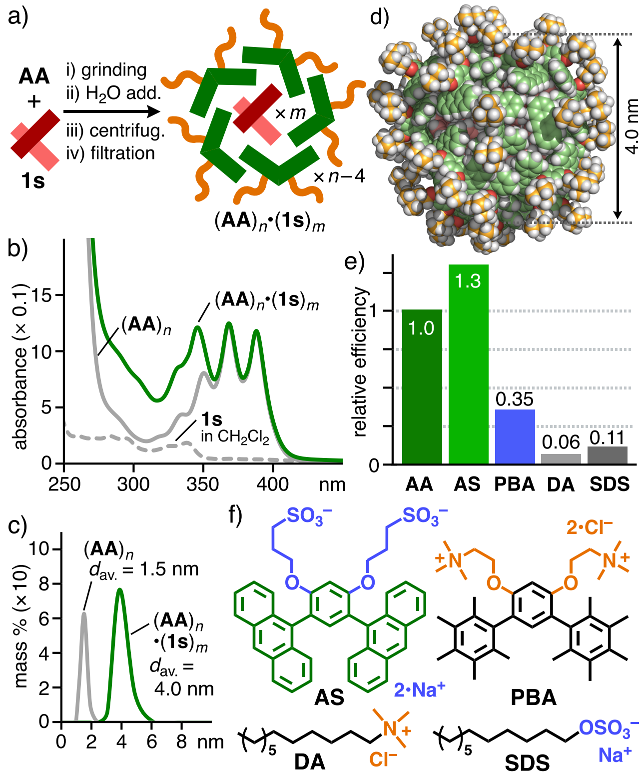


**Figure 2.** a) Formation of $(\mathbf{AA})_n\cdot(\mathbf{1s})_m$ in water through a grinding protocol. b) UV−visible spectra ($H_2O$, r.t., 1.0 mM based on **AA**) of $(\mathbf{AA})_n\cdot(\mathbf{1s})_m$, $(\mathbf{AA})_n$, and **1s** (0.2 mM). c) DLS charts ($H_2O$, r.t., 1.0 mM based on **AA**) of $(\mathbf{AA})_n\cdot(\mathbf{1s})_m$ and $(\mathbf{AA})_n$. d) Optimized structure of $(\mathbf{AA})_{27}\cdot(\mathbf{1s})_{18}$ (MM calculation). e) Relative uptake efficiency of micelles from various amphiphiles toward **1s** in water. f) Aromatic and alkyl amphiphiles studied herein.

Within the polyaromatic shell, the presence of multiple CH-$\pi$ and $\pi-\pi$ interactions in aggregated $(\mathbf{1s})_m$ was also supported by the structure.[15,17] Typical alkyl-based micelles such as $(\mathbf{DA})_n$ and $(\mathbf{SDS})_n$, in contrast, showed inefficient binding ability toward **1s** by the same protocol (~0.1-fold as compared with $(\mathbf{AA})_n$; Figure 2e,f), owing to the lack of host−guest $\pi-\pi$ interactions. Other aromatic micelles $(\mathbf{AS})_n$ featuring hydrophilic sulfonate groups and $(\mathbf{PBA})_n$ featuring hydrophobic pentamethylbenzene panels encapsulated **1s** with high and moderate efficiency relative to that of $(\mathbf{AA})_n$, respectively (Figure 2e).

The chiroptical properties (e.g., CD signal intensity and sign) of **1s** were largely altered upon encapsulation by aromatic micelles at room temperature. The CD spectrum of **1s** in $CH_2Cl_2$ exhibited two negative Cotton effects at 280 and 320 nm. In contrast, that of host−guest composite $(\mathbf{AA})_n\cdot(\mathbf{1s})_m$ in $H_2O$ showed two intense positive Cotton effects at 300 and 340 nm ($\theta_{max}$ = 55 mdeg) as well as an intense negative one at 280 nm, derived from bound $(\mathbf{1s})_m$ (Figure 3a). The negative to positive inversion of the **1s**-based CD bands was thus induced through encapsulation.[18] Weak negative Cotton effects were also detected between 350 and 420 nm ($\theta_{min}$ = −2.1 mdeg), which is in the range of the anthracene-based absorption bands of $(\mathbf{AA})_n$ (Figure 2b), suggesting optical chirality transfer from guest $(\mathbf{1s})_m$ to host $(\mathbf{AA})_n$. To clarify the chirality enhancement of **1s** upon encapsulation, the CD spectrum of $(\mathbf{AA})_n\cdot(\mathbf{1s})_m$ in $CH_3CN$, where the host−guest composite is *fully disassembled* into *n*·**AA** and *m*·**1s**, was


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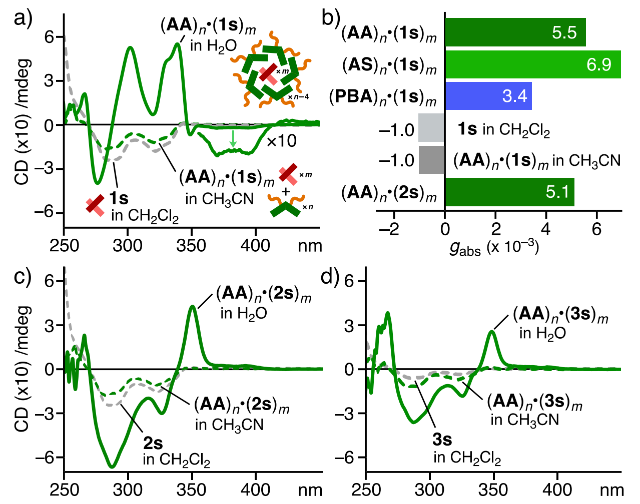


**Figure 3.** a) CD spectra (r.t., 1.0 mM based on **AA**) of $(\mathbf{AA})_n{\cdot}(\mathbf{1s})_m$, **1s** (0.4 mM), and disassembled $(\mathbf{AA})_n{\cdot}(\mathbf{1s})_m$. b) Maximum $g_{abs}$ values ($H_2O$, r.t., 1.0 mM based on amphiphiles) of (**AA** or **AS** or **PBA**)$_n{\cdot}$(**1s** or **2s**)$_m$, **1s**, and disassembled $(\mathbf{AA})_n{\cdot}(\mathbf{1s})_m$. CD spectra (rt, 1.0 mM based on **AA**) of c) $(\mathbf{AA})_n{\cdot}(\mathbf{2s})_m$, **2s** (0.5 mM), and disassembled $(\mathbf{AA})_n{\cdot}(\mathbf{2s})_m$, and d) $(\mathbf{AA})_n{\cdot}(\mathbf{3s})_m$, **3s** (0.3 mM), and disassembled $(\mathbf{AA})_n{\cdot}(\mathbf{3s})_m$.

observed after lyophilization of the aqueous $(\mathbf{AA})_n{\cdot}(\mathbf{1s})_m$ solution. The spectrum shape was comparable to that of free **1s** in $CH_2Cl_2$, and no CD band was detected at 350−420 nm (Figure 3a). Notably, the absolute CD intensity of $(\mathbf{AA})_n{\cdot}(\mathbf{1s})_m$ in $H_2O$ (absolute absorption dissymmetry factor ($|g_{abs}|$) = 5.5 × $10^{-3}$, $\lambda$ = 301 nm) was enhanced by 5.5-fold, as compared to those of **1s** in $CH_2Cl_2$ and disassembled $(\mathbf{AA})_n{\cdot}(\mathbf{1s})_m$ in $CH_3CN$ ($|g_{abs}|$ = 1.0 × $10^{-3}$, $\theta_{min}$ = −17 mdeg, $\lambda$ = 282 nm; Figure 3b).[19] Further CD enhancement of **1s** (6.9-fold) was observed upon encapsulation by sulfonate-based aromatic micelle $(\mathbf{AS})_n$ in $H_2O$ (Figure 2f, 3b, and S12). On the other hand, host−guest composites (**PBA** or **DA** or **SDS**)$_n{\cdot}(\mathbf{1s})_m$ showed weaker CD bands ($\theta_{max}$ = 3−18 mdeg; Figure S12) with moderate $|g_{abs}|$ values (3.4−3.9 × $10^{-3}$) under the same conditions. The observed CD enhancement and inversion of **1s** within $(\mathbf{AA})_n$ stem from the tight aggregation of $m{\cdot}\mathbf{1s}$,[20] accompanying the alteration of the dihedral angle ($\varphi$) of **1s**, in the polyaromatic cavity.[21,22]

Dialkoxy substituents on the binaphthyl largely altered the chiroptical properties of the resultant host−guest composites in water. The CD spectrum of $(\mathbf{AA})_n{\cdot}(\mathbf{2s})_m$, prepared from **AA** and ethoxy derivative **2s** in the same manner as $(\mathbf{AA})_n{\cdot}(\mathbf{1s})_m$,[15] exhibited a strong negative and positive Cotton effect at 280 and 350 nm ($\theta_{min}$ = −67 mdeg), respectively (Figure 3c). The maximum intensity of the absolute CD bands ($|g_{abs}|$ = 5.1× $10^{-3}$, $\lambda$ = 286 nm) was 4.0-fold higher than that of dissociated $(\mathbf{AA})_n{\cdot}(\mathbf{2s})_m$ in $CH_3CN$ ($\lambda$ = 282 nm) and comparable to that of $(\mathbf{AA})_n{\cdot}(\mathbf{1s})_m$ in water (Figure 3b). The CD spectrum of $(\mathbf{AA})_n{\cdot}(\mathbf{3s})_m$ (R = $OCH_2CH_2CH_3$) was similar to that of $(\mathbf{AA})_n{\cdot}(\mathbf{2s})_m$ with weaker intensity ($|g_{abs}|$ = 4.1× $10^{-3}$, $\lambda$ = 286 nm, Figure 3d). Within the aromatic micelle, accordingly, the aggregation-induced chiroptical properties of binaphthyls could be tuned (i.e., ∼3−6 times) by a slight change in the alkoxy substituents.

Next, (1) efficient coencapsulation of axially chiral compounds **2s** (R = $OCH_2CH_3$) with achiral macrocycle dyes, (2) emission enhancement of the coencapsulated dyes, and (3) guest-to-guest optical chirality transfer were demonstrated within aromatic micelle $(\mathbf{AA})_n$. As such an achiral dye, hydrophobic [9]cycloparaphenylene (**CP**, X = H; Figure 4b) was employed to facilitate tight guest−guest

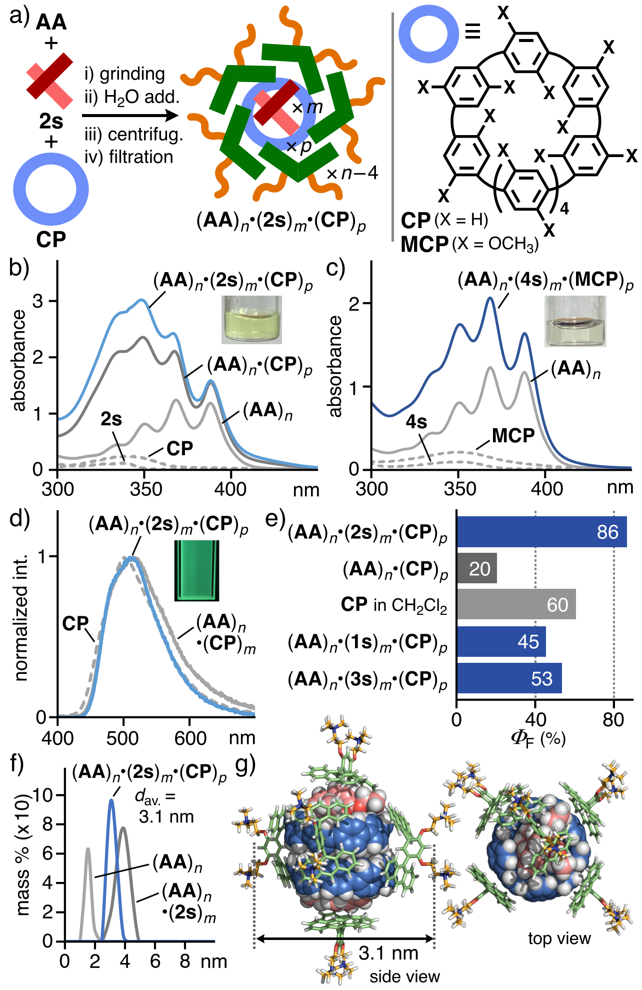


**Figure 4.** a) Formation of $(\mathbf{AA})_n{\cdot}(\mathbf{2s})_m{\cdot}(\mathbf{CP})_p$ in water. UV−visible spectra ($H_2O$, r.t., 1.0 mM based on **AA**) of b) $(\mathbf{AA})_n{\cdot}(\mathbf{2s})_m{\cdot}(\mathbf{CP})_p$, $(\mathbf{AA})_n{\cdot}(\mathbf{CP})_m$, $(\mathbf{AA})_n$, and **CP** (0.01 mM) and **2s** (0.1 mM) in $CH_2Cl_2$, and c) $(\mathbf{AA})_n{\cdot}(\mathbf{4s})_m{\cdot}(\mathbf{MCP})_p$, $(\mathbf{AA})_n$, and **MCP** (0.01 mM) and **4s** (0.1 mM) in $CH_2Cl_2$. d) Fluorescence spectra ($H_2O$, r.t., $\lambda_{ex}$ = 300 nm, 1.0 mM based on **AA**) of $(\mathbf{AA})_n{\cdot}(\mathbf{2s})_m{\cdot}(\mathbf{CP})_p$, $(\mathbf{AA})_n{\cdot}(\mathbf{CP})_m$, and **CP** (0.01 mM) in $CHCl_3$. e) Emission quantum yields ($H_2O$, r.t., $\lambda_{ex}$ = 325, 340, 305 nm) of host−guest composites, and **CP** (0.1 mM). f) DLS charts ($H_2O$, r.t., 1.0 mM based on **AA**) of $(\mathbf{AA})_n{\cdot}(\mathbf{2s})_m{\cdot}(\mathbf{CP})_p$, $(\mathbf{AA})_n{\cdot}(\mathbf{2s})_m$, and $(\mathbf{AA})_n$. g) Optimized structure of $(\mathbf{AA})_6{\cdot}(\mathbf{2s})_2{\cdot}(\mathbf{CP})_2$ (MM calculation).

interactions with **2s** in the macrocyclic cavity. The absorption and emission wavelengths of **CP** are obviously different from those of $(\mathbf{AA})_n$. Coencapsulation of **2s** and **CP** by $(\mathbf{AA})_n$ was carried out through a three-component grinding protocol. A mixture of solids **AA** and **2s** (1.0 $\mu$mol each), and **CP** (0.5 $\mu$mol) was manually ground for 1 min. After the addition of water (1.0 mL) and complete removal of the suspended solid of free **2s** and **CP**, ternary host−guest composite $(\mathbf{AA})_n{\cdot}(\mathbf{2s})_m{\cdot}(\mathbf{CP})_p$ was obtained as a yellow aqueous solution (Figure 4a).[15] The composition and structure of $(\mathbf{AA})_n{\cdot}(\mathbf{2s})_m{\cdot}(\mathbf{CP})_p$ were carefully revealed by a combination of UV−visible, DLS, NMR, and molecular modeling analyses. The UV−visible spectrum of the resultant solution showed broad bands at


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300−370 nm, derived from encapsulated $(\mathbf{2s})_m$ and $(\mathbf{CP})_p$, besides bands at 320−420 nm from $(\mathbf{AA})_n$ (Figure 4b). The DLS analysis indicated the core diameter of the product being 3.1 nm on average (Figure 4f), unlike those of $(\mathbf{AA})_n$ and $(\mathbf{AA})_n{\cdot}(\mathbf{2s})_m$. The average **AA**:**2s**:**CP** ratio of the product was estimated to be 3:1:1 by the $^1$H NMR study (Figure S19b).[15] These results suggested that the obtained composite provides a hydrophobic core, comprising two molecules of **CP** accommodating two molecules of **2s**, surrounded by a polyaromatic shell, formed from six molecules of **AA**, through molecular modeling studies (Figure 4g).[23]

It is noteworthy that the ternary host−guest composite $(\mathbf{AA})_n{\cdot}(\mathbf{2s})_m{\cdot}(\mathbf{CP})_p$ emitted strong green fluorescence derived from bound **CP** in water. In the fluorescence spectrum, intense emission bands were observed at $\lambda_{max}$ = 507 nm with a high quantum yield ($\Phi_F$ = 86%; Figure 4d). The yield is 4.3-fold higher than that of $(\mathbf{AA})_n{\cdot}(\mathbf{CP})_p$ in water ($\Phi_F$ = 20%) and 1.4-fold higher than that of free **CP** in $CHCl_3$ ($\Phi_F$ = 60%; Figure 4e). Ternary host−guest composites $(\mathbf{AA})_n{\cdot}(\mathbf{1s})_m{\cdot}(\mathbf{CP})_p$ and $(\mathbf{AA})_n{\cdot}(\mathbf{3s})_m{\cdot}(\mathbf{CP})_p$ were also prepared using **AA**, **CP**, and **1**/**3s** (R = $OCH_3$/$OCH_2CH_2CH_3$; Figure S29−S33). The resultant composites showed green emission with $\Phi_F$ = 45% ($\lambda_{max}$ = 519 nm) and 53% ($\lambda_{max}$ = 512 nm), respectively (Figure 4e). On the other hand, relatively weak emission ($\Phi_F$ = 10%) was detected from sulfonate-based composite $(\mathbf{AS})_n{\cdot}(\mathbf{2s})_m{\cdot}(\mathbf{CP})_p$ under the same conditions (Figure S33a).[15,10d] The observed emission enhancement within $(\mathbf{AA})_n$ is most probably caused by CH-$\pi$-based guest−guest interactions between **2s** and **CP** (Figure 4g), which suppresses its thermal deactivation through dynamic motion upon excitation.[24] Notably, the quantum yield of $(\mathbf{AA})_n{\cdot}(\mathbf{2s})_m{\cdot}(\mathbf{CP})_p$ ($\Phi_F$ = 86%) represents the quite high value, observed among **CP** reported previously,[25] even under ambient aqueous conditions.

Optical chirality transfer from guests **2s** to **CP** within the discrete aromatic micelle was clearly confirmed by CD and CPL analyses. In the CD spectrum of $(\mathbf{AA})_n{\cdot}(\mathbf{2s})_m{\cdot}(\mathbf{CP})_p$ in water, a new positive Cotton effect was observed at 350−400 nm ($|g_{abs}|$ = 1.4 × $10^{-4}$, $\lambda$ = 368 nm; Figure 5a,e), which coincides with the absorption band of $(\mathbf{CP})_p$ within $(\mathbf{AA})_n$ (Figure 4b), combined with the **2s**-based positive Cotton effect at 330−360 nm. The mirror symmetric CD spectrum ($|g_{abs}|$ = 1.2 × $10^{-4}$) was displayed from its enantiomer $(\mathbf{AA})_n{\cdot}(\mathbf{2r})_m{\cdot}(\mathbf{CP})_p$. The observed **CP**-based bands stem from efficient chirality transfer from **2s**/**r** to **CP** through simple coencapsulation by micelle $(\mathbf{AA})_n$.[26] In contrast, the **CP**-based CD bands hardly appeared in the spectra of $(\mathbf{DA})_n{\cdot}(\mathbf{2s})_m{\cdot}(\mathbf{CP})_p$ and $(\mathbf{AS})_n{\cdot}(\mathbf{2s})_m{\cdot}(\mathbf{CP})_p$ even under the same conditions (Figure 5e and S26b,27b). These results also clarified the exact formation of the guest-within-guest ternary structure (Figure 4g) as a major product. The CPL spectra of $(\mathbf{AA})_n{\cdot}(\mathbf{2s})_m{\cdot}(\mathbf{CP})_p$ and $(\mathbf{AA})_n{\cdot}(\mathbf{2r})_m{\cdot}(\mathbf{CP})_p$ showed roughly symmetric mirror bands in the range between 450 and 660 nm (Figure 5b), which corresponds to the emission band of **CP** (Figure 4d). The absolute emission asymmetry factors ($|g_{lum}|$) of the host−guest composites were estimated to be 2.0 × $10^{-4}$ ($\lambda$ = 510 nm; Figure 5f). The observed CPL, derived from guest-to-guest optical chirality transfer in host compounds, is quite uncommon in various host−guest CPL systems reported previously.[27]

To deepen the understanding of the observed chirality transfer, chiroptical studies of various host−guest composites were examined under the same aqueous conditions. The **CP**-based CD bands of $(\mathbf{AA})_n{\cdot}(\mathbf{1s}$ or $\mathbf{2s}$ or $\mathbf{3s})_m{\cdot}(\mathbf{CP})_p$ at 360 nm

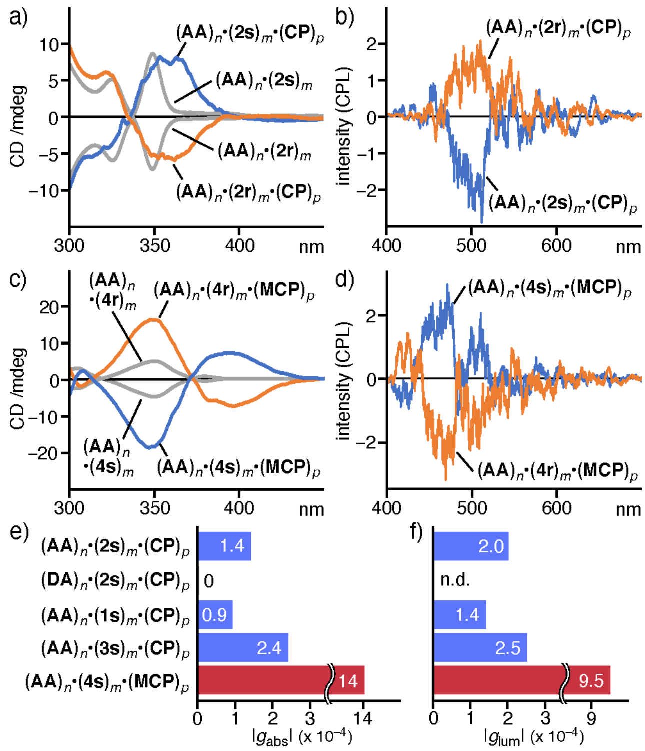


**Figure 5.** a) CD spectra ($H_2O$, r.t., 1.0 mM based on **AA**) of $(\mathbf{AA})_n{\cdot}(\mathbf{2s}$ or $\mathbf{2r})_m{\cdot}(\mathbf{CP})_p$ and $(\mathbf{AA})_n{\cdot}(\mathbf{2s}$ or $\mathbf{2r})_m$, and b) their selected CPL spectra ($\lambda_{ex}$ = 325 nm). c) CD spectra ($H_2O$, r.t., 1.0 mM based on **AA**) of $(\mathbf{AA})_n{\cdot}(\mathbf{4s}$ or $\mathbf{4r})_m{\cdot}(\mathbf{MCP})_p$ and $(\mathbf{AA})_n{\cdot}(\mathbf{4s}$ or $\mathbf{4r})_m$, and d) their selected CPL spectra ($\lambda_{ex}$ = 300 nm). e) **CP**/**MCP**-based maximum $|g_{abs}|$ and f) $|g_{lum}|$ values ($H_2O$, r.t., $\lambda_{ex}$ = 340, 305 nm) of various host−guest composites.

indicated that binaphthyl with longer alkoxy groups (R = $OCH_2CH_2CH_3$; $|g_{abs}|$ = 2.4 × $10^{-4}$) is more effective in the chirality transfer than that with shorter ones (R = $OCH_3$; $|g_{abs}|$ = 0.9 × $10^{-4}$; Figure 5e). No guest−guest interaction was found between **2s** and **CP** without **AA** in solution (Figure S28).[15] The CD spectrum of $(\mathbf{PBA})_n{\cdot}(\mathbf{2s})_m{\cdot}(\mathbf{CP})_p$ also displayed a **CP**-based band at ∼400 nm ($|g_{abs}|$ = 0.6 × $10^{-4}$; Figure S22), suggesting the importance of the polyaromatic host framework in this system. Size/shape complementarity and CH-$\pi$-based guest−guest interactions in the cyclic guest cavity are essential for the observed chirality transfer because no dye-based CD band was detected from $(\mathbf{AA})_n{\cdot}(\mathbf{2s})_m{\cdot}$([12]cycloparaphenylene)$_p$ under the same conditions (Figure S23), owing to its large macrocyclic framework (1.7 nm in diameter). Composites $(\mathbf{AA})_n{\cdot}(\mathbf{1s}$ or $\mathbf{3s})_m{\cdot}(\mathbf{CP})_p$ exhibited CPL bands at 450−660 nm (Figure 5e and S45,S47), with medium $|g_{lum}|$ values in water ($|g_{lum}|$ = 1.4 and 2.5 × $10^{-4}$, respectively). Furthermore, efficient guest-to-guest chiroptical transfer could be also applied to sterically hindered, multi-methoxy functionalized [9]cycloparaphenylene (**MCP**; Figure 4a, right) upon coencapsulation with diamino binaphthyls **4s**/**r** without bulky substituents (R = $NH_2$; Figure 1e).[12b,15] An intense CD band at 370−450 nm ($|g_{abs}|$ = 1.4 × $10^{-3}$, $\lambda$ = 396 nm) and CPL bands at 400−600 nm ($|g_{lum}|$ = 9.5 × $10^{-4}$, $\lambda$ = 476 nm) were notably observed in the chiroptical spectra of $(\mathbf{AA})_n{\cdot}(\mathbf{4s}$ or $\mathbf{4r})_m{\cdot}(\mathbf{MCP})_p$ in water (Figure 5c and 5d, respectively). The large enhancement of the observed $|g_{abs}|$ and $|g_{lum}|$ values (i.e., 3.8 to 15.6-fold) through guest replacement from achiral dyes **CP** to **MCP** is most likely attributed to the


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enhanced conformational rigidity of the macrocyclic framework (e.g., induced planar chirality) by the sterically demanding methoxy groups (Figure 5e,f).

In summary, we have succeeded in the effective enhancement and transfer of the chiroptical properties of axially chiral binaphthyls within nonchiral aromatic micelles, with dimensions of ∼3−4 nm. Both phenomena were generated upon simple encapsulation with or without cycloparaphenylenes under ambient aqueous conditions. Large CD enhancement of the binaphthyl compounds was observed in the cavity. Coencapsulation of the chiral compounds with the achiral macrocycles led to the selective formation of guest-within-guest ternary composites, providing macrocycle-based, high emissivity, as well as CPL activities, via unusual "guest-to-guest" chirality transfer. Thanks to the finite, adaptable host frameworks of the aromatic micelles and high accessibility to axially chiral compounds, we believe that the present, simple coencapsulation strategy could be applied for wide-ranging nonchiral dyes and metal-complexes[28] to generate new chiroptical materials and chiral catalysts, respectively, without elaborate chiral functionalization on the guest frameworks.

## ■ ASSOCIATED CONTENT

### Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacsau.4c01229.

Experimental procedures; NMR, MS, IR, UV−visible, fluorescence, DLS, CD, CPL, and calculation data (PDF)

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### Notes

The authors declare no competing financial interest.

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(15) See the Supporting Information.

(16) The alkoxy groups are essential for the efficient encapsulation of **1**. Binaphthol (R = OH; Figure 1e) was hardly bound by $(\mathbf{AA})_n$ even under various conditions.

(17) $^1$H NMR spectrum of $(\mathbf{AA})_n\cdot(\mathbf{1s})_m$ in $D_2O$ (Figure S7a) showed significantly broadened guest signals, indicating suppressed guest motion through strong host−guest interactions in the cavity. The host−guest composite was stable even under high dilution conditions (i.e., < 0.01 mM based on **AA**; Figure S11).

(18) The absorption bands of **1s** were red-shifted upon encapsulation by $(\mathbf{AA})_n$ due to its aggregation in the cavity. The **1s**-based Cotton effects of $(\mathbf{AA})_n\cdot(\mathbf{1s})_m$ in water are similar to those of solid **1s** (Figure S13).[15]

(19) The CD spectrum of $(\mathbf{AA})_n\cdot(\mathbf{1r})_m$, prepared from **AA** and enantiomer **1r**, showed the mirror image of that of $(\mathbf{AA})_n\cdot(\mathbf{1s})_m$ (Figure S13).[15]

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(21) For the mechanistic study, the inversed and enhanced Cotton effects of **1s** were suggested by the dihedral angle-dependent DFT analysis (Figure S18).[15] The computed CD spectra slowed a positive ($\varphi$ = 60−70°) or negative bond ($\varphi$ = 80−100°) at ∼ 310 nm.

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(23) To further support the formation of the guest-within-guest structures in $(\mathbf{AA})_n\cdot(\mathbf{1\text{-}3s/r})_m\cdot(\mathbf{CP})_p$, host−guest composites $(\mathbf{AA})_n\cdot(\mathbf{5s})_m\cdot(\mathbf{CP})_p$ and $(\mathbf{AA})_n\cdot(\mathbf{2s})_m\cdot(\mathbf{6})_p$ were prepared using much bulkier (*S*)-2,2'-dimethoxy-6,6'-diphenyl-1,1'-binaphthyl (**5s**) and acyclic *para*-hexaphenylene (**6**), respectively, in the same way.[15] Their CD spectra showed no or quite weak band derived from the guest-to-guest chirality transfer within $(\mathbf{AA})_n$ (Figure S49 and S50).

(24) Emission lifetime of $(\mathbf{AA})_n\cdot(\mathbf{2s})_m\cdot(\mathbf{CP})_p$ in $H_2O$ (9.8 ns) is slightly longer than that of **CP** in $CHCl_3$ (7.6 ns) under ambient conditions (Figure S25b). The suppressed aggregation of **CP**s via uptake of **2s** in the micelle is another possible reason. The ternary composite was also stable under dilution conditions (i.e., < 0.01 mM based on **AA**; Figure S33b).

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