ORIGINAL ARTICLE

Circularly polarized luminescence (CPL) characteristics of hydrophobic pyrene derivatives/γ-cyclodextrin (γ-CD) complexes in aqueous solution dissolved by grinding

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Abstract

Circularly polarized luminescence (CPL) organic dyes are currently receiving a great interest, but there are still not many reported observations of CPL spectra of hydrophobic dyes from aqueous solution. We have prepared hydrophobic pyrene derivatives and dissolved them into aqueous solutions with γ-cyclodextrin (γ-CD) by using grinding technique. Among these derivatives, (pyrene-1-carbonyl)serine (PySer) forms a spatially restricted dimer in the hydrophobic chiral cavity of γ-CD and exhibits excimer emission with a high quantum yield of $\Phi_f = 0.68$. In addition, circular dichroism and CPL signals were induced for the complex. The strong g_{CPL} value of $g_{CPL} = +2.2 \times 10^{-3}$ was obtained, which may be attributed to the interaction between the hydroxyl groups in the side chain of PySer with those of γ-CD and it strengthens the chiral dimeric structure.

Graphic abstract

PySer/γ-cyclodextrin (γ-CD) complex exhibits excimer emission ($\Phi_f = 0.68$) with g_{CPL} value of $g_{CPL} = +2.2 \times 10^{-3}$.
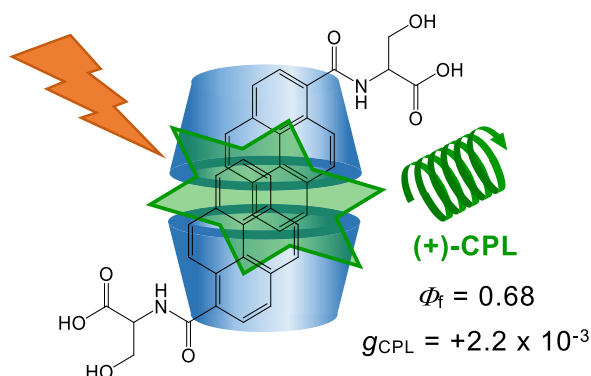
Keywords Circularly polarized luminescence (CPL) · Fluorescence · Pyrene · Grinding · Cyclodextrin

Introduction

Organic dyes that emit circularly polarized luminescence (CPL) have attracted a great attention due to their photophysical behavior and have been actively studied in chiroptic materials science [1–6]. Basically, CPL can be obtained from linearly polarized light by using a circularly polarized light filter, but the light intensity and energy efficiency are greatly reduced in this case [7]. To avoid this problem, rigid chiral skeletons for organic dyes have been designed so far that emit selectively positive (+) and negative (−) CPL, respectively. However, preparation of such a chiral chromophore is often difficult, because of the limited availability of materials as well as the multi-step synthesis and time-consuming chiral separation processes [8].

On the other hand, many chromophores that release CPL from organic solvents have been reported, while there are

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limited studies on effective CPL release in aqueous solvent [9–12]. Pyrene is one of typical polycyclic aromatic hydrocarbons, showing an unique photophysical property [13–18]. Since the 1980 s, pyrene has been known to interact with the cavity of γ-cyclodextrin (γ-CD) through a hydrophobic interaction to produce CPL as a result of encapsulated pyrene excimer formation [14–17, 19, 20]. Two pyrene derivatives are asymmetrically twisted by forming a 2:2 pyrene/γ-CD complex in aqueous solution and chirality is induced from achiral pyrene molecules by complexation with chiral γ-CD. For limited examples, Kano et al. indicated that the 2:1 or 2:2 pyrenesulfonic acid/γ-complex gave CPL with the g_{CPL} value of 1.5×10^{-2} [15]. Recently, Inouye et al. demonstrated the amphiphilic double alkynylpyrene molecule forms a 2:2 encapsulated complex with γ-CD and its strong CPL with $g_{CPL} = 1.5 \times 10^{-2}$ appears in water. In the 2:2 γ-CD-encapsulated alkynylpyrene pair reported by Inouye et al., the introducing bulky substituents at the ends of the pyrene molecules acted as stoppers in the rotaxane structure [19]. Therefore, it is expected that inclusion of achiral fluorescent molecule into γ-CD cavity can be utilized to develop novel CPL materials. Furthermore, the introduction of alkyl side chains with various structures into the pyrene scaffold may regulate the pyrene-γ-CD complexation and the CPL property by forming non-covalent interactions between the side chain and the hydroxyl group of the γ-CD.

Pyrene is a hydrophobic fluorescent molecule and is generally difficult to use in water. Mechanical grinding of hydrophobic aromatic compound mixed with γ-CD as a solid state is a promising technique for dissolving the molecule in water [21, 22]. Shinkai et al. also reported solubilization of hydrophobic porphyrin and 2,3,6-tri-O-methyl-β-cyclodextrin complex into water by using grinding technique [23]. In order to develop water soluble CPL materials comprising achiral or racemic hydrophobic pyrene derivatives and chiral γ-CD, we have prepared hydrophobic pyrene derivatives, N-(2-aminoethyl)pyrene-1-carboxamide (Pyen), 2-(pyrene-1-carboxamido)acetic acid (PyGly),

2-(pyrene-1-carboxamido)propanoic acid (PyAla), (pyrene-1-carbonyl)serine (PySer), and 3-(pyrene-1-carboxamido) propanoic acid (PyβAla) as shown in Fig. 1. It is noted that the pyrene derivatives used here are divided in two categories. One is pyrene grafted with achiral side chain and another is racemic mixture of pyrene grafted with chiral side chain. In the latter case, we used racemic amino acids instead of enantiomers throughout this study. These pyrene derivatives have low solubility in water by themselves. Our study aims at the following points; (1) Prepare a variety of new hydrophobic pyrene derivatives and show that the grinding technique is effective in dissolving their γ-CD complexes in aqueous solution for the first time, (2) Clarify their photophysical absorption and emission excimer properties by experimental spectroscopic measurements and theoretical DFT calculations, (3) Systematically study the combination of achiral or racemic hydrophobic pyrene derivatives/γ-CD complexes to develop new water-soluble CPL materials, and (4) Regulation the pyrene-γ-CD complexation and the CPL property by forming non-covalent interactions between the pyrene side chain and the γ-CD.

Results and discussion

Syntheses and structures of pyrene derivatives

Pyen, PyGlyEt, PyAlaEt, PySerMe and PyβAlaEt were synthesized by condensation of 1-pyrene carboxylic acid with *tert*-buthyl-N-(2-aminoethyl)carbamate, glycine ethyl ester hydrochloride, alanine ethyl ester hydrochloride, serine methyl hydrochloride, and β-alanine ethyl ester hydrochloride (Scheme S1 in supplementary materials). Abbreviations used are PyGlyEt = ethyl-2-(pyrene-1-carboxamido)acetate, PyAlaEt = ethyl-2-(pyrene-1-carboxamido)propanoate, PySerMe = methyl-3-hydroxy-2-(pyrene-1-carboxamido) propanoate and PyβAlaEt = ethyl-3-(pyrene-1-carboxamido)prpanoate. PyGly, PyAla, PySer, and PyβAlaEt were

Fig. 1 Structures of Pyen, PyGlyEt, PyGly, PyAlaEt, PyAla, PySerMe, PySer, Py*b*AlaEt, and Py*b*Ala
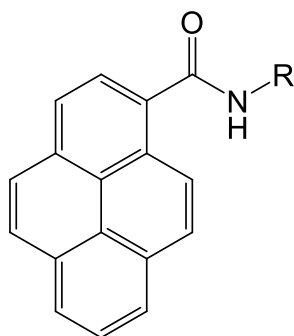
Pyen : R = CH$_2$-CH$_2$-NH$_2$

PyGlyEt : R = CH$_2$-C(=O)OEt

PyGly : R = CH$_2$-C(=O)OH

PyAlaEt : R = CH(CH$_3$)-C(=O)OEt

PyAla : R = CH(CH$_3$)-C(=O)OH

PySerMe : R = CH(CH$_2$OH)-C(=O)Me

PySer : R = CH(CH$_2$OH)-C(=O)OH

PyβAlaEt : R = CH$_2$-CH$_2$-C(=O)OEt

PyβAla : R = CH$_2$-CH$_2$-C(=O)OH

synthesized by hydrolysis of PyGlyEt, PyAlaEt, PySerMe, and PyβAlaEt, respectively. Details of the synthetic procedure and identification of pyrene derivatives are also given in the supplementary materials (Figs. S1–S4 and Tables S1–S4).

Preparation of water soluble pyrene/γ-CD by grinding

The preparation of the hydrophobic pyrene/γ-CD complex was conducted according to the literature [23]. γ-CD (9.0×10^{-6} mol) and pyrene derivative (4.5×10^{-6} mol) were mixed and ground for 30 min in an agate mortar. Then, 5.0 mL of phosphate buffer (1.0 mM, pH = 7.0) was added and sonicated for 15 min. The mixture was stirred for 12 h. After removal of the insoluble materials by filtration using a membrane filter, the solution was obtained and used for spectroscopic measurements. The concentrations of pyrene/γ-CD complexes in aqueous solution were estimated from absorption spectra using molar extinction coefficient, ε, of the corresponding pyrene moiety in DMF (Figs. S5 and S6). The ε values for Pyen, PyGly, PyAla, PySer, and PyβAla are $\varepsilon_{342} = 3.61 \times 10^4$ M^{-1} cm^{-1}, $\varepsilon_{340} = 4.12 \times 10^4$ M^{-1} cm^{-1}, $\varepsilon_{340} = 3.55 \times 10^4$ M^{-1} cm^{-1}, $\varepsilon_{341} = 4.13 \times 10^4$ M^{-1} cm^{-1}, and $\varepsilon_{341} = 3.93 \times 10^4$ M^{-1} cm^{-1}, respectively. In order to eliminate the solubility differences based on the changes in pH of water, we used a phosphate buffer (1.0 mM, pH = 7.0) in this study. The pHs of the solutions were confirmed by pH meter and were within pH = 7.0 ± 0.2 during the measurements. We note that this grinding method is a necessary procedure to make the hydrophobic pyrene/γ-CD complexes water-soluble at the concentrations written in the experimental conditions.

Photophisical properties of pyrene/γ-CD complexes

The UV and emission spectral measurements of the prepared pyrene/γ-CD complexes were conducted as shown in Figs. S5-S6 and Fig. 2, respectively. Five pyrene derivatives, Pyen, PyGly, PyAla, PySer, and PyβAla were well solubilized in aqueous solution by grinding with γ-CD. For the fluorescence spectral measurements, a 2 mm length of quartz cuvette was used to avoid the influence of inner filter effects. As depicted in Fig. 2, PyGly/γ-CD, PyAla/γ-CD, PySer/γ-CD, and PyβAla/γ-CD, show clear excimer fluorescence around 500 nm, accompanying with a very weak shoulder peak around 400 nm. Pyen/γ-CD also has fluorescence peaks at 507 nm and 402 nm, respectively. The latter peak was assigned to the monomer fluorescence. Then, we have determined the absolute emission quantum yield for all complexes and they are listed in Table 1. The PySer/γ-CD composite showed the highest value of $\Phi_f = 0.68$. These results indicate that the carboxy group on the pyrene side
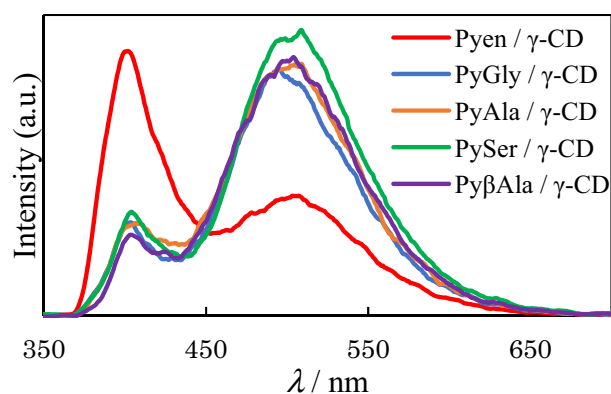

Fig. 2 Emission spectra of Pyen/g-CD, PyGly/g-CD, PyAla/g-CD, PySer/g-CD, and PybAla/g-CD in a N$_2$-saturated 1 mM phosphate buffer(pH 7.0) at room temperature

Table 1 Emission properties of pyrene/γ-CD complexes in a N$_2$-saturated 1 mM phosphate buffer (pH 7.0) at room temperature

Complex	Conc. M^{-1}	Emission (Monomer)		Emission (Excimer)	Φ_f [a]
		λ_{ex} nm^{-1}	λ_{em} nm^{-1}	λ_{em} nm^{-1}	
Pyen/γ-CD	2.55×10^{-4}	342	402	507	0.55
PyGly/γ-CD	3.05×10^{-4}	340	403	494	0.63
PyAla/γ-CD	4.51×10^{-4}	340	407	509	0.60
PySer/γ-CD	3.15×10^{-4}	341	404	509	0.68
PyβAla/γ-CD	5.17×10^{-4}	341	404	504	0.57

[a]The emission quantum yield was calculated as the absolute quantum yield

chain is important for dimer formation in γ-CD cavity to present excimer fluorescence in a buffer solution. On the other hand, Pyen has an amino group at the end of the side chain and it is considered to be positively charged in water at pH = 7.0. It was suggested that there are different inclusion mechanisms for positively or negatively charged guest molecule with CD [24]. An inclusion complex of positively charged molecule with CD indicates that the cationic guest molecule can slip through a CD cavity to form pseudorotaxane structure, even if the complex is thermodynamically stable [25]. Because of such difference in the inclusion mechanism, we consider that only Pyen is less likely to form the pyrene dimer complex in a buffer solution at present.

Emission lifetimes of pyrene/γ-CD complexes

Next, we have measured the fluorescence lifetimes of Pyen/γ-CD, PyGly/γ-CD, PyAla/γ-CD, PySer/γ-CD, PyβAla/γ-CD complexes in water and each of the corresponding pyrene monomers in DMF (Fig. 3 and Fig. S7). The excitation wavelength was $\lambda_{ex} = 330$ nm which was in the absorption of pyrene. For the pyrene/γ-CD complexes,

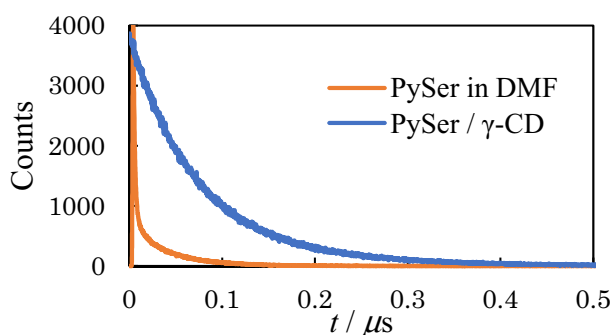**Fig. 3** Emission decay of PySer/*g*-CD (3.15×10^{-4} M) in a N_2-saturated 1 mM phosphate buffer at pH7.0 (l_{ex} = 330 nm, $l_{em} > 450$ nm) and PySer in a N_2-saturated DMF at room

Table 2 Emission lifetimes of pyrene derivatives/γ-CD complexes in a N_2-saturated 1 mM phosphate buffer (pH 7.0) at room temperature ($\lambda_{ex} = 330$ nm, $\lambda_{em} > 450$ nm)

Complex	Emission lifetime ns^{-1} (A / %)			χ^2
	τ_1	τ_2	τ_{ave}	
Pyen/γ-CD	40.1 (26)	110 (74)	91.7	1.03
PyGly/γ-CD	47.4 (47)	116 (53)	83.5	1.05
PyAla/γ-CD	69.4 (68)	144 (32)	93.0	1.03
PySer/γ-CD	61.7 (58)	116 (42)	84.4	1.05
PyβAla/γ-CD	66.6 (46)	129 (54)	100	1.07

the single photon counting was carried out using a > 450 nm cut filter and the excimer lifetimes were observed. It has been known that the formation of a 2:2 inclusion complex of pyrene with γ-CD can inhibit the quenching by molecular oxygen and thus provides a longer fluorescence lifetime [20, 26]. The decay profile was analyzed as a sum of two exponentials using the emission intensity (I_t), time (t), lifetime (τ) and the fractional contribution (A) by the following equation.

$$I_t = A_1 \exp\left(-t/t_1\right) + A_2 \exp\left(-t/t_2\right)$$

Table 2 summarizes the lifetimes of τ values and the average of τ_1 and τ_2 is represented as τ_{ave}. In comparison to pyrene monomers, it is shown that pyrene/γ-CDs have longer lifetimes in a phosphate buffer (Fig. 3, Fig. S7, and Table S5). We consider the lifetime of Pyen, PyGly, PyAla, PySer, and PyβAla in aqueous solution is prolonged by the formation of γ-CD complexes and the excimer fluorescence appears from the hydrophobic γ-CD environment. These τ_{ave} values are comparable to the reported lifetimes for the excimer fluorescence of 2:2 pyrene/γ-CD complexes [20, 26]. From the fluorescence spectra in Fig. 2, Pyen/γ-CD shows relatively weaker dimer fluorescence than the other

PyGly/γ-CD, PyAla/γ-CD, PySer/γ-CD, and PyβAla/γ-CD systems. However, there is not much different from the fluorescence lifetime measurements. Although the estimated lifetimes suggest multiple components, the inclusion mechanism of Pyen/γ-CD is not clear at the present stage.

Density functional theory (DFT) calculations of pyrene monomer and dimer

In order to present energy diagrams (eV) for the ground state (GS) and singlet excited state (ES), the molecular structure calculations of monomer and dimer were performed with density functional theory (DFT) using the Gaussian16 program package [27]. The Becke three parameters hybrid exchange [28] and the Lee-Yang-Parr correlation functionals (B3LYP) [29, 30] were used with the 6–31 + G* basis set including the PCM [31–33] solvent effect (solvent = H_2O). The initial structures of the calculation were based on those obtained by X-ray crystallographic analysis. The structures of PySerMe, PyβAla, and PyAlaEt were determined by X-ray crystallography. The figures of the capped sticks of the crystal structures were plotted by Mercury in Figs. S1–S4, and their crystallographic data were summarized in Tables S1–S4. In the case of PyAla and PySer, we have not obtained their crystal structures. Then, the calculations were performed based on the crystal structures of PyAlaEt and PySerMe, respectively. Time dependent DFT (TD-DFT) was applied to interpret comparisons between the GS and ES geometries. The fluorescence energies (2.97 eV, 2.96 eV, 2.96 eV, 2.62 eV, 2.73 eV, and 2.75 eV) calculated for PySerMe (monomer), PyβAla (monomer), PyAlaEt (monomer), PySerMe (dimer), PyβAla (dimer), and PyAlaEt (dimer) are relatively good agreement with the experimental ones for pyrene/γ-CD complex in water (3.07 eV for PySer (monomer), 3.07 eV for PyβAla (monomer), 3.05 eV for PyAla (monomer), 2.44 eV for PySer (dimer), 2.46 eV for PyβAla (dimer), and 2.44 eV for PyAla (dimer)) as shown in Fig. 4. We note that PyAlaEt did not give the GS geometry in the dimer state. Since the pyrene/γ-CD complexation reactions are dynamic in solution, it is considered that both monomer and dimer complexes for the pyrene/γ-CD systems are possible.

Circular dichroism and CPL spectra of pyrene/γ-CD complexes

The pyrene/γ-CD complexes that produce excimer fluorescence are considered to be chiral in the ground state, due to the overlap of pyrene rings within the γ-CD cavity. Therefore, we measured the circular dichroism spectra as displayed in Fig. 5. For the five pyrene/γ-CD complexes for which excimer fluorescence was observed, the circular dichroism spectra showed strong cotton effects on the
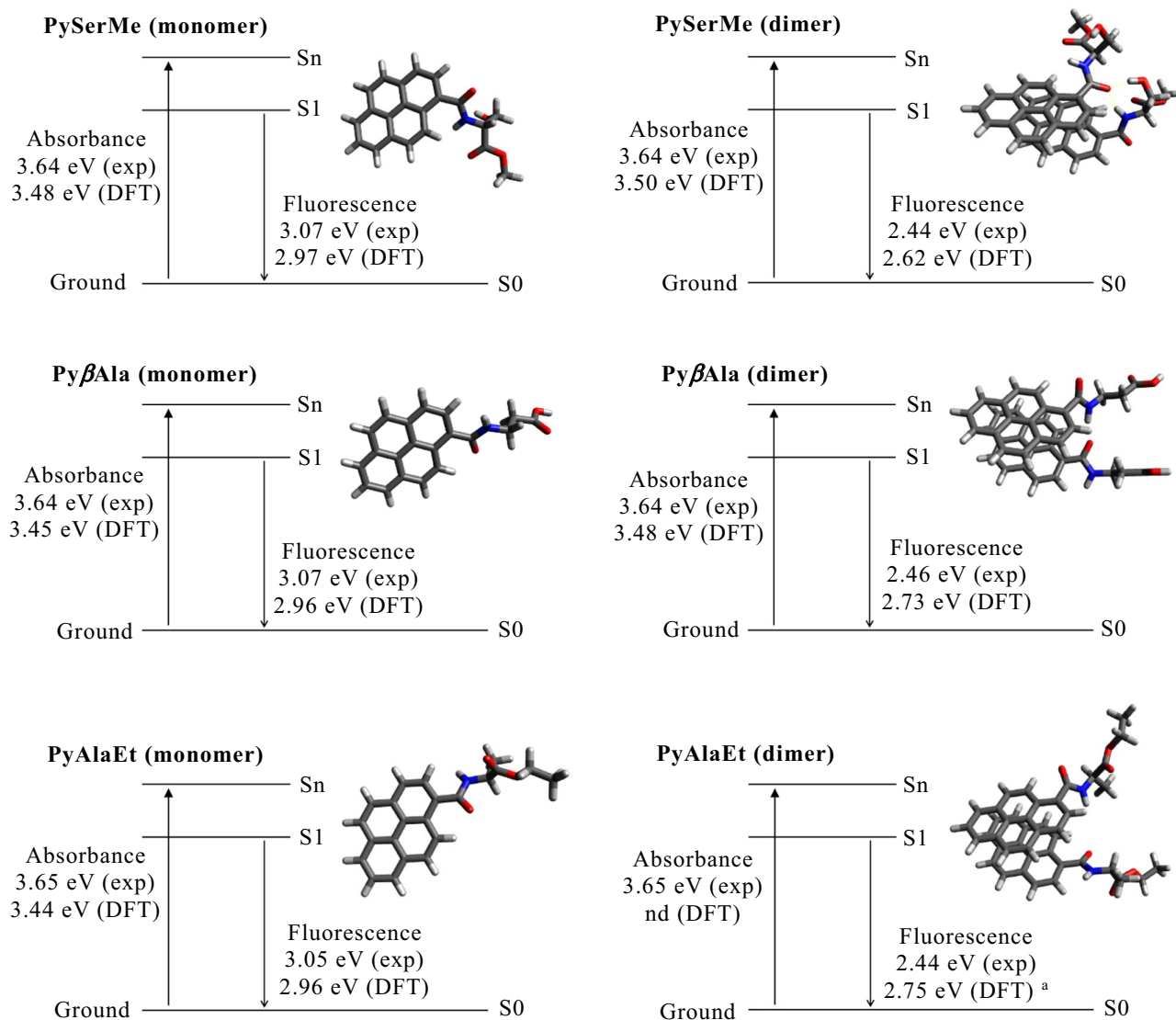
Fig. 4 Energy diagrams for PySerMe (monomer), PySerMe (dimer), PyβAla (monomer), PyβAla (dimer), PyAlaEt (monomer), and PyAlaEt (dimer). [a]Calculated by the comparison with two monomers

absorption region of pyrene in 280–430 nm (Table 3). The induced weak sign of the first cotton band was negative around 420 nm. It is also known that when two left-handed chromophores are located in close proximity to each other, the circular dichroism spectra from the longer wavelengths show a negative (420 nm) to positive (340 nm) to negative (280 nm) cotton effect based on the exciton chirality method [34]. This predicts that all of these pyrene molecules are twisted in the left chirality interacted with the γ-CD cavity in the ground state (Fig. 6).

Next, we also measured CPL spectra of the five complexes where CD spectra were observed (Fig. 7). In order to quantitatively assess the CPL characteristics, we used the dimensionless Kuhn's anisotropy factor g_{CPL} in the photoexcited state as the following equation.

$$g_{CPL} = (I_L - I_R)/[1/2\,(I_L + I_R)]$$

Here, I_L and I_R denote the recorded intensities of left- and right-handed CPL under the excitation of unpolarized light, respectively. From Table 4, Pyen/γ-CD, PyAla/γ-CD, PySer/γ-CD, and PyβAla/γ-CD showed positive CPL, and their anisotropic factors were $|g_{CPL}| = 2.7 \times 10^{-4}$, 8.3×10^{-4}, 2.2×10^{-3}, and 5.2×10^{-4}, respectively. On the other hand, PyGly/γ-CD showed a negative CPL with an anisotropic factor of $|g_{CPL}| = 1.1 \times 10^{-4}$. In the case of PyGly, the steric hindrance of the pyrene side chain is smaller than that of the other pyrene derivatives. This is thought to make PyGly easier to move within the cavity of γ-CD and the twist of the PyGly dimer is likely to be inverted in the excited state. The sign of the CPL signals around 405 nm was negative

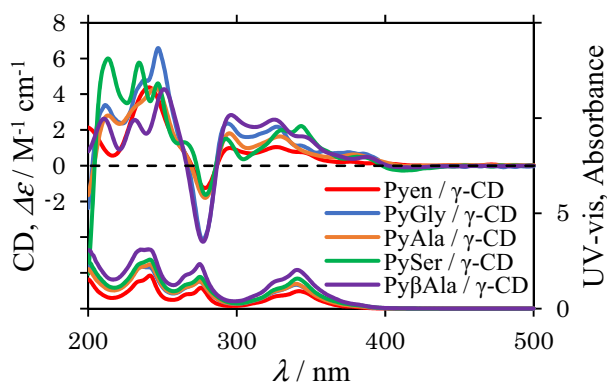**Fig. 5** Circular dichroism (CD, upperpanel) and UV–Vis (lower panel) spectra of Pyen/*g*-CD, PyGly/*g*-CD, PyAla/*g*-CD, PySer/*g*-CD, and Py*b*Ala/*g*-CD in1 mM phosphate buffer (pH 7.0) at room temperature

and found to be consistent with that of the first CD cotton band. The largest CPL spectra an anisotropic factor of $|g_{CPL}| = 2.2 \times 10^{-3}$ were observed for PySer/γ-CD. This value is comparable to those of the previously reported ones for pyrene/γ-CD complexes observed in water [15, 16, 20,

35]. This is probably because the hydroxyl group on the Ser residue forms a hydrogen bond with the hydroxyl groups of γ-CD, which fixes the torsional structure and stabilizes the PySer/γ-CD inclusion complex.

Reversibility of PySer/γ-CD complex

The inclusion between pyrene and γ-CD is reversible in aqueous solution, while the reversible equilibrium between γ-CD and pyrene does not occur in the previous rotaxane-type system reported by Inouye et al. [19]. In the present study, among the five pyrene-CD complexes, the PySer/γ-CD showed the clear dimer fluorescence and the largest quantum yield. The CPL measurement also showed the largest g value of 2.2×10^{-3}. We assume that the strong luminescence property of the PySer/γ-CD is probably because the hydroxyl group on the Ser residue forms a hydrogen bond interaction with the γ-CD, which fixes the torsional structure and stabilizes the PySer/γ-CD inclusion complex. In order to confirm the reversible equilibrium of the pyrene and γ-CD complex, we have then selected the PySer/γ-CD to various-temperature ^{1}H-NMR

Table 3 Circular dichroism spectral properties of Pyen/γ-CD, PyGly/γ-CD, PyAla/γ-CD, PySer/γ-CD, and PyβAla/γ-CD in 1 mM phosphate buffer (pH = 7.0) at room temperature

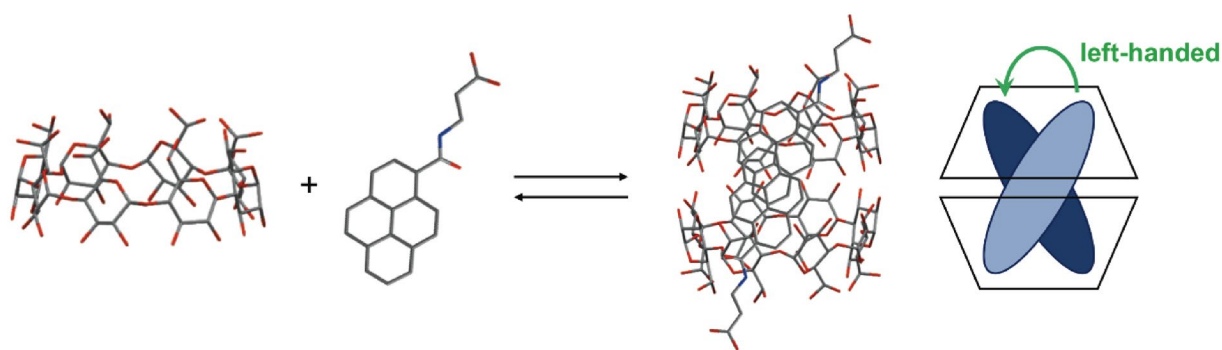| Complex	Conc. M^{-1}	λ_1 nm^{-1} (sign)	λ_2 nm^{-1} (sign)	λ_3 nm^{-1} (sign)
Pyen/γ-CD	2.55×10^{-4}	279 (−)	342 (+)	428 (−)
PyGly/γ-CD	3.05×10^{-4}	275 (−)	340 (+)	413 (−)
PyAla/γ-CD	4.51×10^{-4}	275 (−)	340 (+)	416 (−)
PySer/γ-CD	3.82×10^{-4}	275 (−)	341 (+)	412 (−)
PyβAla/γ-CD	5.17×10^{-4}	275 (−)	341 (+)	419 (−)

Fig. 6 Schematic illustration for possible configuration in pyrene/γ-CD systems
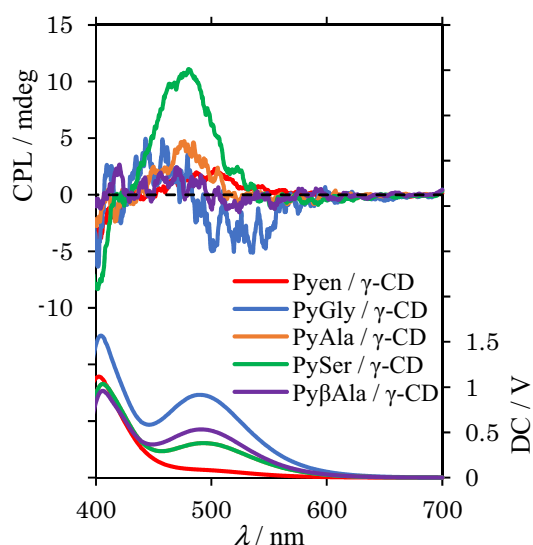
Fig. 7 CPL (upper panel) and PL (lower panel) spectra of Pyen/g-CD, PyGly/g-CD, PyAla/g-CD, PySer/g-CD, andPybAla/g-CD in1 mM phosphate buffer (pH 7.0) at room temperature (l_{ex} = 350nm)

measurements in D_2O (Fig. 8). The temperatures were set at room temperature, 30 °C, 40 °C, 50 °C, 60 °C, 70 °C, and 80 °C, respectively. At room temperature and 30 °C, the up-field shifts of all the protons of γ-CD were observed in the PySer/γ-CD complex, accompanied with new peaks of the H_1, H_2, and H_4 protons of γ-CD (green circle in Fig. 8a, b) [36]. This may be due to the ring current effect of the pyrene upon its interaction with γ-CD. On the other

hand, the broadening of the H signals on the pyrene ring of PySer suggests that the two pyrene rings are in close proximity within γ-CD. At 40 °C, the protons of γ-CD are coalesced, and at higher temperatures, the H signals on the pyrene ring of PySer were slightly sharpened (Fig. 8c–g). Comparing the spectra of γ-CD only and PySer/γ-CD at 80 °C, it was found that the H_3 and H_5 proton signals of γ-CD were upfield shifted (Fig. S8 and Table S6). Comparison at 80 °C between the PySer and PySer/γ-CD also shows that the PySer/γ-CD gives a considerably more complex signal in the pyrene moiety. These data indicate that pyrene and γ-CD interact with each other by forming PySer/γ-CD complex even at high temperature of 80 °C. After raising the temperature to 80 °C, the temperature was lowered again to room temperature and then the ^{1}H NMR signals were almost identical to the original ones (Fig. S9).

Next, fluorescence spectra were measured in the PySer/γ-CD complex at variable temperatures. Fluorescence spectral results are shown in Fig. 9a and the color change under UV light (365 nm) is also shown in Fig. 9b. As the temperature increased, the intensity of excimer fluorescence gradually decreased and the intensity of monomer fluorescence increased. Furthermore, the green fluorescence changed to blue one with increasing temperature. There seems to be an isoemissive point at 455 nm in Fig. 9a, suggesting the conversion of dimer to monomer complex of the PySer/γ-CD.

Therefore, these results support that the formation of pyrene/γ-CD complexes is reversible. It is considered that

Table 4 CPL properties of Pyen/γ-CD, PyGly/γ-CD, PyAla/γ-CD, PySer/γ-CD, and PyβAla/γ-CD in 1 mM phosphate buffer (pH = 7.0) at room temperature

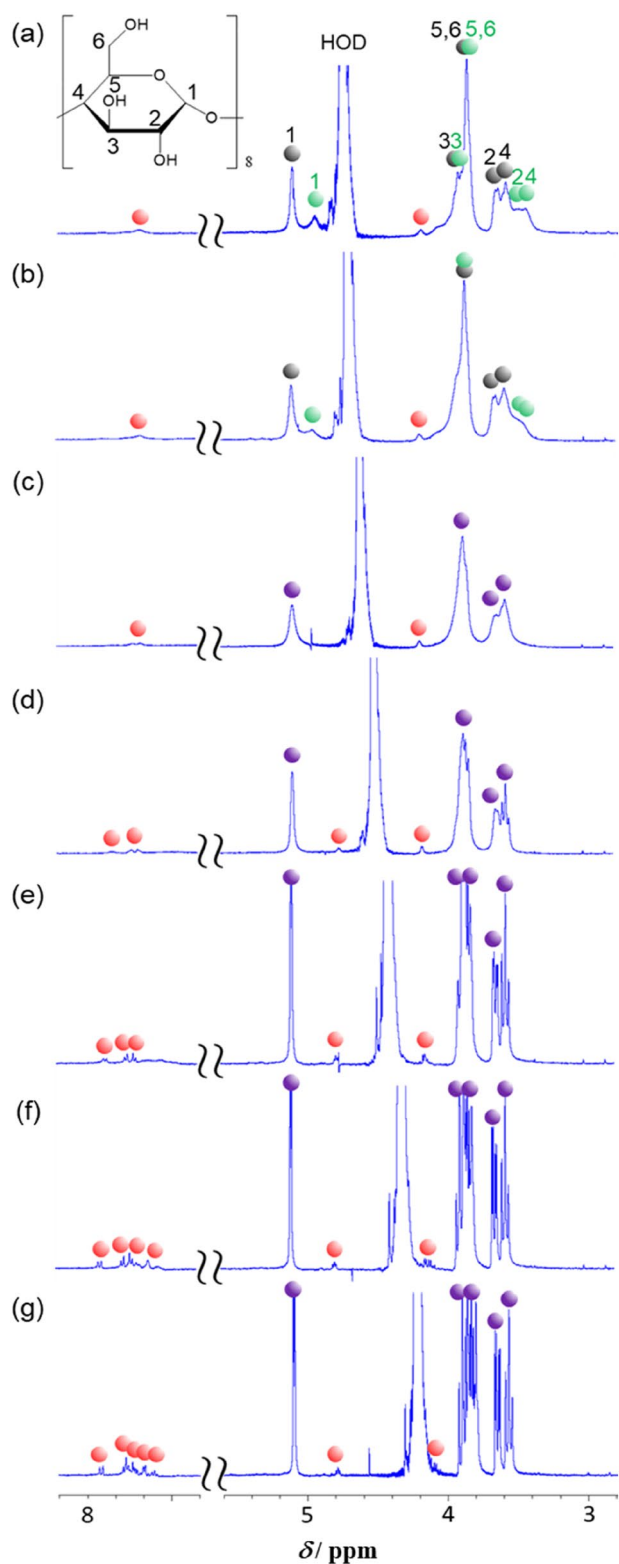| Complex	Conc. M^{-1}	λ_{ex} nm^{-1}	λ_1 nm^{-1} (sign)	λ_2 nm^{-1} (sign)	$\|g_{CPL}\|$
Pyen/γ-CD	5.25×10^{-4}	350	405 (−)	502 (+)	2.7×10^{-4}
PyGly/γ-CD	2.87×10^{-4}	350	402 (−)	490 (−)	1.1×10^{-4}
PyAla/γ-CD	4.51×10^{-4}	350	404 (−)	476 (+)	8.3×10^{-4}
PySer/γ-CD	3.15×10^{-4}	350	405 (−)	480 (+)	2.2×10^{-3}
PyβAla/γ-CD	5.17×10^{-4}	350	404 (−)	461 (+)	5.2×10^{-4}

Fig. 8 Partial ^{1}H NMR spectra of PySer/γ-CD (4.9×10^{-4} M) in D$_2$O at **a** room temperature, **b** 30 °C, **c** 40 °C, **d** 50 °C, **e** 60 °C, **f** 70 °C, and **g** 80 °C (black circle : γ-CD, red circle : PySer, green circle : PySer/γ-CD, and purple circle : γ-CD + PySer/γ-CD). (Color figure online)

the pyrene and γ-CD can form 1:1, 1:2, 2:1 and 2:2 complexes in aqueous solution depending on the molecular structures of pyrene derivatives. Since the complexation reactions are dynamic in solution, it is difficult to determine the stoichiometric ratios of complexes by job plot. Due to our experimental limitations, the stoichiometry of the PySer/γ-CD complex and the abundance of 1:1, 1:2, 2:1 and 2:2 complexes have not been determined at the moment. The details including the inclusion and chiral recognition mechanisms of γ-CD with chiral D- or L-derivative will be reported elsewhere in the future. However, we have demonstrated various CPL characteristics of pyrene/γ-CD complexes comprising achiral or racemic hydrophobic pyrene derivatives and chiral γ-CD in aqueous solution. Our strategy could be utilized to develop novel water-soluble CPL materials by using γ-CD and pyrene composites.
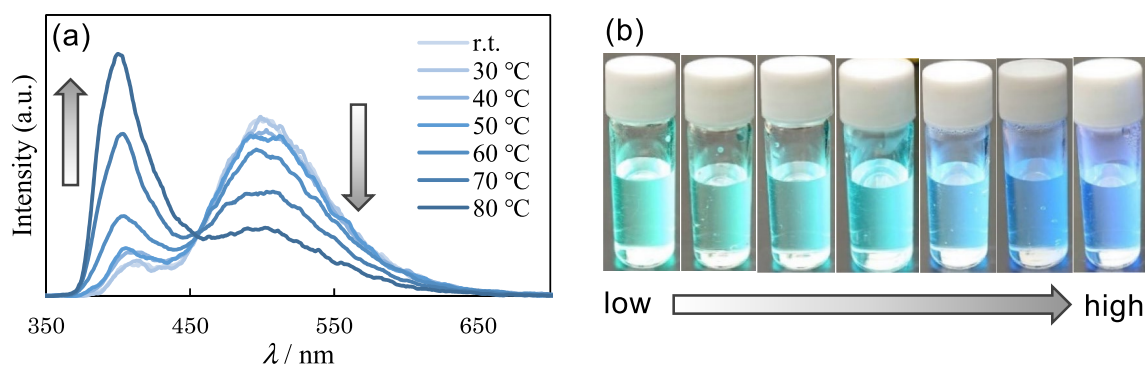
Fig. 9 **a** Emission spectra of PySer/γ-CD (4.9×10^{-4} M) in a N$_2$-saturated 1 mM phosphate buffer (pH 7.0) at r.t., 30 °C, 40 °C, 50 °C, 60 °C, 70 °C, and 80 °C and **b** photograph of PySer/γ-CD in a N$_2$-saturated 1 mM phosphate buffer (pH 7.0) upon UV irradiation (365 nm) at r.t., 30 °C, 40 °C, 50 °C, 60 °C, 70 °C, and 80 °C

Conclusion

We have synthesized hydrophobic pyrene derivatives and prepared new several pyrene/γ-CD composites in aqueous solution dissolved by grinding. Among these derivatives, excimer fluorescence was observed for Pyen/γ-CD, PyGly/γ-CD, PyAla/γ-CD, PySer/γ-CD and PyβAla/γ-CD complexes in aqueous solution. Their photophysical absorption and emission properties were investigated by experimental spectroscopic measurements and theoretical DFT calculations. In addition, circular dichroism and obvious CPL signals were induced for these complexes. PySer forms a spatially restricted dimer in the hydrophobic cavity of γ-CD and exhibits excimer emission with a high quantum yield of $\Phi_f = 0.68$ and the g_{CPL} value of $g_{CPL} = +2.2 \times 10^{-3}$. This may be attributed to the interaction between the hydroxyl groups in the side chain of PySer with those of γ-CD and it strengthens the chiral dimeric structure.

Declarations

Conflict of interest The authors declare no conflict of interest.

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