Chiral stacking of cyanine or porphyrin as cationic fluorescent dyes in the presence of anionic polysaccharide of hyaluronic acid

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Abstract

Cyanine dye or porphyrin are part of an important family of fluorophores, which have been widely used for photosensitization and optical recording materials. We compared herein the aggregation behaviors of two types of cationic dyes of cyanine or porphyrin in the presence of hyaluronic acid, which contains D-glucuronic acid as anionic helical polysaccharide. UV-Vis absorption and photoluminescence spectra of those aqueous solutions revealed that fluorescent dyes of cyanine form H- and J-aggregates in the presence of hyaluronic acid. In particular, photoluminescent quenching through the H- and J-aggregates was observed in the mixture of anionic hyaluronic acid and the cationic cyanine dyes. On the contrary, increment of the intensities of the emission was confirmed in the mixture of porphyrin-hyaluronic acid through the effective interaction between the cationic porphyrin and anionic hyaluronic acid, which was confirmed by remarkable split-Cotton effects of induced circular dichroism in the visible region, though the UV-Vis spectra of porphyrin with hyaluronic acid did not show any sign of aggregation of porphyrin itself. Further addition of hyaluronic acid resulted in the decrease of the extent of the induced circular dichroism, though photoluminescent intensity was kept without quenching. It was also confirmed that the light scattering could be detected only when the remarkable split-Cotton effects were observed. Therefore, cationic porphyrin and anionic hyaluronic acid form complex and the complex might assemble to show the light scattering, though the single molecule of porphyrin was surrounded by polysaccharides and isolated without dye-aggregation.

Keywords Fluorescent dye · Polysaccharide · Photoluminescence · Induced chirality

1 Introduction

Cyanine dyes are polymethine dyes consist of two nitrogen centers joined by a conjugated chain of odd number of methine carbons or a conjugated system of double bonds [1–3]. Although 3,3'-diethyldithiadicarbocyanine iodide (DTDC), one of the cyanine dyes, is an achiral molecule, DTDC formed chiral H-aggregate on duplex DNA [4–9]. Porphyrins are planar macrocyclic molecules containing four pyroles connected in ring fashion through four

methine carbons at their α -positions [10]. They are part of an important family of fluorophores, which have been widely used for photosensitization and optical recording materials [2, 3, 10]. Porphyrins are well known to form chiral aggregate in the presence of DNA and act as the stabilizer for the secondary structure of nucleic acid [11–15]. 5, 10, 15, 20-Tetrakis (1-methylpyridinium-4-yl) porphyrin p-toluene sulfonate (TMPyP) is one of the water soluble cationic porphyrins.

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Hyaluronic acid (HA) is one of interesting helical polysaccharides that has been utilized as a scaffold for dyes through the electrostatic molecular interactions, which resulted in induction of circular dichroism (CD) in the visible region [16–19]. We previously studied utilization of anionic HA as a scaffold to improve alignment of cationic fluorescent dyes such as 3,3'-diethyl-9-methylthiacarbocyanine (DMTC) [16], DTDC [17], 3,3'-diethylthiacarbocyanine iodide (DTC) [17], 3,3'-diethylthiacyanine iodide (DTTHC) [17], 1-pyrenemethylamine hydrochloride (PyrMA) [18, 19], and TMPyP [18, 19]. HA binds as the ligand to CD44 that is overexpressed in cancer cells [20, 21]. Therefore, delivery of anticancer drugs or diagnostic drugs for cancer have been studied by using the specific binding properties of HA [22–24]. In particular near-infrared (NIR) fluorescence imaging agents that specifically accumulate in tumors are needed to those cancer drugs [23–25]. In this context, cyanine dyes and porphyrins derivatives are widely applicable to NIR fluorescence imaging agents [25]. We compared herein the two types of cationic dyes: DTDC or TMPyP, which has different chemical structure, behaviors with HA containing D-glucuronic acid (Scheme 1) in aqueous solution in terms of their spectroscopic properties in their UV–Vis absorption and CD spectra in addition to photoluminescence (PL).

2 Materials and methods

2.1 Materials and preparations

DTDC and TMPyP were purchased from Sigma-Aldrich Corporate. HA powder (HA-Q, extracted from cockscomb. Mw: 530,000–1,330,000 g mol⁻¹, Japanese Standards of Quasi-Drug Ingredients (JSQI): Sodium Hyaluronate (1, Ingredient Code: 520893) were provided by Kewpie Corporation. HA (or TMPyP) was dissolved in buffer solution [pH=3.2 with HCOOH/KOH, 4.9 with CH₃COOH/KOH, 7.0 with Na₂HPO₄/KH₂PO₄, and 9.0 with Na₂B₄O₇/H₃BO₃] or water. DTDC was dissolved in methanol. Those solutions stored at 4 °C in a refrigerator.

2.2 UV–Visible, CD, PL spectroscopy and DLS measurement

UV–Visible absorption spectra were measured using Ultrospec 4000 UV/Visible Spectrophotometer (Pharmacia Biotech) and CD spectra were measured with J-725 CD spectrometer (JASCO, Japan). PL spectra was measured using FP-8600 Spectrophotometer (JASCO, Japan). Dynamic light scattering (DLS) was measured with DLS spectrophotometer (Otsuka Electronics Co., Ltd. DLS-8000DH).

Samples for those measurements were put in a quartz cuvette with 10 mm optical path length.

3 Results

3.1 UV–Visible and PL spectra of DTDC with HA

Figure 1 shows UV–Vis absorption and PL spectra of DTDC and HA in 2.4 vol% methanol-buffer (pH=7.0).

Addition of HA (0–50 unit μmol L⁻¹) to DTDC led to the decrease of the absorbance at 650 nm and appeared broad absorption band ranging from 500 to 850 nm (Fig. 1a). The absorption spectra have three absorption peaks at 556 nm, 650 nm and 800 nm. The absorbance at 650 nm corresponds to the DTDC monomer. While DTDC forms H- (556 nm) and J-aggregates (800 nm) in the presence of HA [17]. Emission peak intensity at 673 nm of DTDC gradually decreased with increasing [HA] from 2 to 10 unit μmol L⁻¹, while it remained almost constant (viz. saturated) when [HA] was 10 to 50 unit μmol L⁻¹ as shown in Figs. 1b and 2b.

3.2 UV–Visible, PL, CD spectra and DLS of TMPyP with HA

Figure 3 shows UV–Vis absorption (a), PL (b) spectra of TMPyP and HA in water. Absorption peaks observed at 430, 528, 562, 598, and 645 nm are assigned to be TMPyP. Addition of HA, the absorption peak of the Soret band of TMPyP resulted in small (~ 3 nm) red shift (Figs. 3a and S1).

Figure 4 shows CD spectra of TMPyP and HA in water.

In the CD spectra, negative split Cotton effect was observed in 390–460 nm, which might be derived from the excitonic interaction of TMPyP molecules themselves (Fig. 4). This negative Cotton effect indicated maximum intensity when [HA] was 30 unit μmol L⁻¹ as shown in Fig. 5.

Excess amount of HA reduced the CD intensity. Therefore, most effective interaction between TMPyP and HA was occurred when [HA] was 30 unit μmol L⁻¹, and further addition of HA distracted the interaction. This is similar trend observed as the changes of emission peak intensity in the region of 600–900 nm (Fig. 3b). The intensity at 675 nm and 720 nm of TMPyP with HA gradually increased with increasing [HA] from 5 to 30 unit μmol L⁻¹, though the intensity at 675 nm reduced remarkably when [HA] was 40 to 100 unit μmol L⁻¹ (Fig. 5b).

Figure 6 indicates UV–Vis absorption (a) and PL (b) spectra of TMPyP and HA in buffer solution.

There are no remarkable changes in the profiles of the absorptions (Fig. 6a). Although CD intensity in the region of 200–250 nm, which is ascribed to the helical structures

Scheme 1 Chemical structures of DTDC (a), TMPyP (b), and HA (c)

of HA was observed in every sample, there is no CD in the visible region of 390–460 nm (the data not shown) except when the solvent was water (Fig. 4).

We have measured DLS of TMPyP ($10 \mu\text{mol L}^{-1}$) with HA ($0\text{--}100 \text{ unit } \mu\text{mol L}^{-1}$) in water. The light scattering

was detected only when the concentrations of HA were 20, 30, and $40 \text{ unit } \mu\text{mol L}^{-1}$ though the scattering intensities were not so high ranging from 550 to 1027 cps under these conditions. On the other hand, further addition of HA into TMPyP did not show the light scattering. In

Fig. 1 **a** UV-Vis absorption and **b** PL spectra of DTDC ($10 \mu\text{mol L}^{-1}$) and HA ($0\text{--}50 \text{ unit } \mu\text{mol L}^{-1}$) in 2.4 vol% methanol-buffer ($\text{pH}=7.0$). Excitation wavelength (λ_{ex}) was 615 nm

Fig. 2 **a** Absorbance changes of DTDC ($10 \mu\text{mol L}^{-1}$) with HA ($0\text{--}50 \text{ unit } \mu\text{mol L}^{-1}$) at 556 nm (H-aggregates), 650 nm (Monomer), 800 nm (J-aggregates) in 2.4 vol% methanol-buffer ($\text{pH}=7.0$).

b PL intensity changes of DTDC ($10 \mu\text{mol L}^{-1}$) with HA ($0\text{--}50 \text{ unit } \mu\text{mol L}^{-1}$) at 673 nm in 2.4 vol% methanol-buffer ($\text{pH}=7.0$). Excitation wavelength (λ_{ex}) was 615 nm

addition to this, DTDC ($10 \mu\text{mol L}^{-1}$) with HA ($0, 10$ and $50 \text{ unit } \mu\text{mol L}^{-1}$) did not show any light scattering.

4 Discussion

4.1 UV-Visible spectra and PL spectra of DTDC with HA

Since HA one unit $\mu\text{mol L}^{-1}$ contains one carboxyl group, the ratio of anion of HA to cation of DTDC is 1: 1. In UV-Vis absorption and PL spectra, when [HA] is more than 10 unit $\mu\text{mol L}^{-1}$ against $10 \mu\text{mol L}^{-1}$ DTDC, the intensities of

the UV-Vis absorption spectra and the emission spectra were kept constant (Fig. 2).

Seifert et al. reported that DTDC formed H-aggregates in the presence of DNA, and DTDC with DNA caused only the decrease of the emission peak [4]. PL is often quenched at high concentrations of luminophores known as “aggregation-caused quenching” (ACQ) [26]. ACQ occurs when luminophores contain planar π -conjugated aromatic rings, which aggregate through strong π - π stacking interaction [26]. Although DTDC formed H-aggregates with DNA [4], DTDC formed not only H-aggregates but also J-aggregates with HA. Furthermore, decrease of the emission intensity at 673 nm without the appearance of new bands was

Fig. 3 UV-Vis absorption (**a**) and PL (**b**) spectra of TMPyP ($10 \mu\text{mol L}^{-1}$) and HA ($0\text{--}100 \text{ unit } \mu\text{mol L}^{-1}$) in water. λ_{ex} was 440 nm

Fig. 4 CD spectra of TMPyP ($10 \mu\text{mol L}^{-1}$) and HA ($0\text{--}100 \text{ unit } \mu\text{mol L}^{-1}$) in water

observed. Since the lifetime of the exciton self-trapped (EST) state of the cyanine J-aggregate in aqueous solution is ranged in several hundred of picosecond [27], the fluorescence quenching as mentioned above might be caused by the exciton–exciton annihilation of the J-aggregate of cyanine dye [28]. In addition, the aggregation of DTDC depends on the dispersion ability of the cyanine dye itself in the mixed solution of DTDC and HA and higher PL intensity was obtained when the molecular weight of HA was small (unpublished data). In other words, such quenching of the PL at around 673 nm was remarkable in the case of

larger molecular weight of HA. Therefore, PL-quenching at around 673 nm observed with increasing the concentration of HA from 2 to $10 \text{ unit } \mu\text{mol L}^{-1}$ might be ascribed to ACQ, which is caused by the formation of both H- and J-aggregates of DTDC nearby HA (Fig. 2).

4.2 UV-Visible, PL, CD spectra and DLS of TMPyP with HA

Geier and Sasaki reported that porphyrin-helical peptide conjugate has the induced band in the Soret region

Fig. 5 **a** Molar ellipticity $[\theta]$ at 437 nm of TMPyP ($10 \mu\text{mol L}^{-1}$) with HA ($0\text{--}100 \text{ unit } \mu\text{mol L}^{-1}$) in water. **b** PL intensity changes of TMPyP ($10 \mu\text{mol L}^{-1}$) with HA ($0\text{--}100 \text{ unit } \mu\text{mol L}^{-1}$) at 675 nm and 720 nm in water. λ_{ex} was 440 nm

Fig. 6 UV-Vis absorption (**a**) and PL (**b**) spectra of TMPyP ($10 \mu\text{mol L}^{-1}$) and HA ($30 \text{ unit } \mu\text{mol L}^{-1}$) in buffer solution (pH = 3.2, 4.9, 7.0). λ_{ex} was 440 nm

in 10 mM phosphate buffer (pH = 7) [29]. The absorption peak (λ_{max}) of the Soret band was broadened and shifted by changing the amount of trifluoroethanol (TFE) as follows: λ_{max} at 430 nm in 10% TFE/buffer, 418 nm in 15% TFE/buffer, 415 nm in 20% TFE/buffer, and 414 nm in >30% TFE/buffer [29]. Therefore, single molecule of porphyrin combined with helical peptide shows induced circular dichroism (ICD) in the Soret region under these conditions. While in the case of the combination of the cationic porphyrin (TMPyP) and the anionic polysaccharide (HA) in this study, although the absorption peaks (λ_{max}) of the Soret band of TMPyP with or without HA have no

remarkable changes ($\sim 3 \text{ nm}$), CD and PL spectra of TMPyP changed remarkably in the visible region with increment of HA concentration. These results suggest that single molecule of (viz. monomeric) TMPyP might interact with HA. Split emission peaks of 675 nm, which is assigned to be Q(0,0) [30] and 720 nm as Q(0,1) [30] are ascribed to two equilibrium states of inner pyrrole protons of TMPyP tautomers. Since TMPyP has four anions per one molecule, TMPyP has four sites to interact with one unit of HA. Two PL peaks at 675 nm and 720 nm increased with increasing the [HA] from 5 to 30 $\text{unit } \mu\text{mol L}^{-1}$ as shown in Fig. 5b. Khurana et al. reported that TMPyP in the presence of

β -Cyclodextrin (β -CD) showed similar trend of PL spectral changes [31]. Moreover, the averaged lifetime of the photoexcited singlet state of TMPyP was extended from 5.2 ns (Free TMPyP) to 11.0 ns (TMPyP- β -CD) [31]. In this context, the increment of those PL intensities of porphyrin in the presence of HA is probably ascribed to the enhancement of the hydrophobic atmosphere, which might suppress the non-radiative deactivation. On the other hand, the intensity at 675 nm decreased by further addition of [HA] more than 40 unit $\mu\text{mol L}^{-1}$ though another PL at 720 nm still increased slightly. Similar trend in the CD spectra of TMPyP and HA in water was observed in the Soret band of 390–460 nm (Figs. 4, 5a) as described above.

We have also measured DLS of TMPyP ($10 \mu\text{mol L}^{-1}$) with HA (0 – $100 \text{ unit } \mu\text{mol L}^{-1}$) in water. It was found that the light scattering could be observed only when the concentrations of HA were 20, 30, and $40 \text{ unit } \mu\text{mol L}^{-1}$ though the scattering intensities were not so high under these conditions. Further addition of HA into TMPyP did not show any light scattering. In this context, even when the UV-Vis spectra of TMPyP with HA do not show any sign of aggregation of porphyrin itself, complex of TMPyP and HA might form and assemble when [HA] was ranged in 20 – $40 \text{ unit } \mu\text{mol L}^{-1}$. Therefore, the negative split Cotton effect of TMPyP/HA was observed under these conditions (Fig. 4) and both a decrease of the CD intensities, and a quenching of emission occurs by further addition of HA, above 1:3 TMPyP/HA molar ratio (blue lines in Fig. 5a, b) were observed.

On the other hand, CD intensity in the region of 200 – 250 nm (negative), which is ascribed to the helical structures of HA gradually increased with increasing the concentration of HA. Similar extent of the CD intensity of HA-TMPyP at 210 nm was observed to that of HA without TMPyP (Fig. S2).

Furthermore, cationic TMPyP does not interact with anionic HA in buffer electrostatically though it can interact in water. Emission profiles of TMPyP with HA in buffer (Fig. 6) are similar to that of TMPyP itself (viz. without HA as shown in Fig. 4). While fluorescence spectra of TMPyP with HA in water show relatively higher intensities of the emission peak at around 675 nm (Fig. 5b), which probably corresponds to the effective electrostatic interaction between TMPyP and HA.

5 Conclusions

Anionic polysaccharide of HA incorporated with cationic fluorescent dyes of DTDC or TMPyP has been prepared and investigated the spectroscopic properties. It was found that cyanine dyes form H- and J-aggregates with HA. PL-quenching at around 673 nm might correspond

to ACQ through predominant formation of the H- and J-aggregates of DTDC in the presence of HA. On the other hand, TMPyP-HA mixture has chirality with remarkable split-Cotton effects in the visible region and PL intensity at 675 nm might be reflected by the assembling behavior of TMPyP-HA complexes of cationic TMPyP and anionic HA, though the UV-Vis spectra of TMPyP with HA did not show any sign of aggregation of porphyrin itself. The increment of the PL intensities of porphyrin in the presence of HA is probably ascribed to the enhancement of the hydrophobic atmosphere, which might suppress the non-radiative deactivation. Both a decrease of the CD intensities, and a quenching of emission occurs by further increasing the HA concentration, above 1:3 TMPyP/HA molar ratio were observed. Therefore, through the electrostatic interactions between cationic TMPyP and anionic HA, single molecule of porphyrin was surrounded by polysaccharides and isolated without dye-aggregation. Consequently, although cyanine dye aggregated in the presence of hyaluronic acid and ACQ was observed, single porphyrin interacted with hyaluronic acid electrostatically with induced chirality and discrete fluorophore surrounded by the polysaccharide kept the strong PL intensity.

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Compliance with ethical standards

Conflicts of interest The authors declare that they have no conflict of interest.

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