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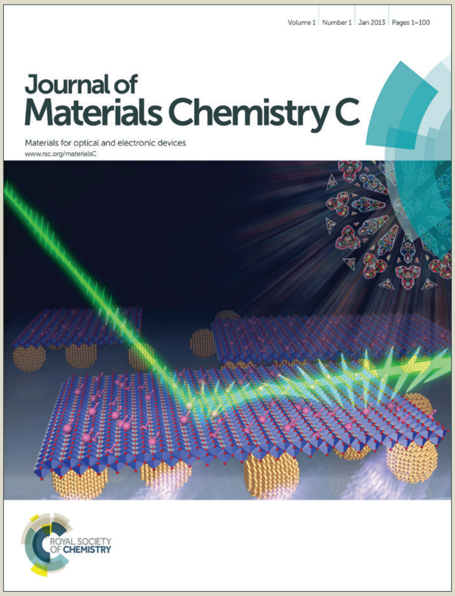

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Molecular Recognition Directed Supramolecular Control over Perylene-bisimide Aggregation Resulting in Aggregation Induced Enhanced Emission (AIEE) and Induced Chiral Amplification

Bappaditya Roy,[a] Takao Noguchi,[a,b] Youichi Tsuchiya,[b] Daisuke Yoshihara,[b] Tasuhiro Yamamoto,[b] and Seiji Shinkai*[a,b,c]

[a] Institute for Advanced Study, Kyushu University, 744 Moto-oka, Nishi-ku, Fukuoka 819-0395, Japan
[b] Nanotechnology Laboratory, Institute of Systems, Information Technologies and Nanotechnologies (ISIT), 4-1 Kyudai-Shinmachi, Nishi-ku, Fukuoka 819-0388, Japan
[c] Department of Nanoscience, Faculty of Engineering, Sojo University, 4-22-1 Ikeda, Nishi-ku, Kumamoto 860-0082, Japan

E-mail: shinkai_center@mail.cstm.kyushu-u.ac.jp

Fax: (+81)92-805-3814

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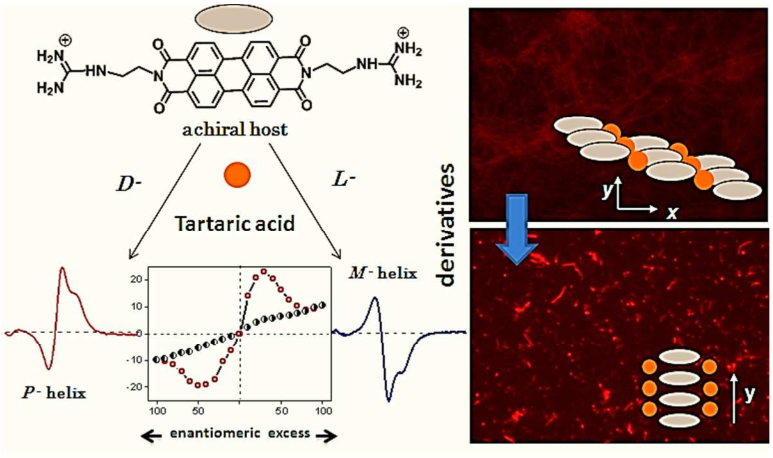


Achiral functional perylene recognizes only dibenzoyl tartaric acid (*D*/*L*) among others by expressing different self-assembled structures, and the selectivity is further voyaged to chiral amplification in the enantiomeric excess experiment

Abstract

Recognition directed spontaneous assembly formation has been used to build-up a sensory system with perylene bis-guanidinium, PBG which presented great responsibility towards chiral guest sensing. Based on the structural modification in the chiral guest molecules, PBG can selectively recognize dibenzoyl tartaric acid, DBTA among other tartaric acids (TA), resulted in explicit read-out of the molecular information *via* generation of the characteristic induced circular dichroism spectra for *D*- and *L*-enantiomers. The binding ability depends only on the substituents in the TA, and the local guidances play an important role in structure formation. The bulky substituents in TA can lead to induce chirality into the cofacial perylene stacks by generating an active angle between the successive transition dipoles. The induced helical sense was found to exhibit efficient chiral amplification with a sigmoidal change (*i.e.* according to sergeants-and-soldiers effect) in the enantiomeric excess plot. The diversity in physical properties was further entertained by the preparative method, and the heating-cooling method, compared to the simple mixing method, is able to show aggregation induced fluorescence enhancement which was used to fabricate highly efficient fluorescent solid in a supramolecular way even from a perylene-based dye.

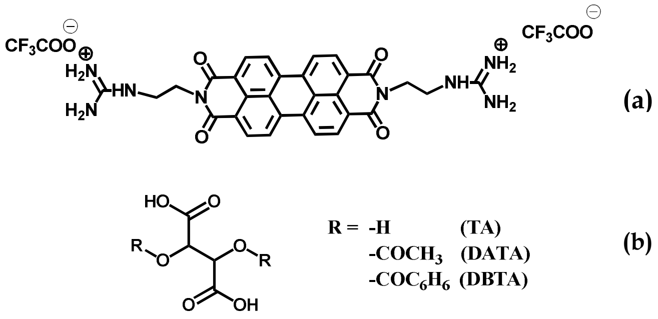
Introduction

Recognition processes occurring at the molecular level may lead to a change in the material level by expressing the molecular information through the spectroscopic window.[1] Most of the chiral guests, in demand, cannot express themselves in a range of available analytical tools. In order to address this disadvantage, discovery and production of optical sensors as references have been getting more interest.[2] In a host-guest mechanistic approach, in this context, there is a great responsibility of the molecular-level chiral guest molecules to employ the material-level helix-sense in the self-assembled structure. It has now become apparent that in achiral molecules, a subtle interplay of non-covalent interactions in a non-symmetric way is sufficient to generate and/or amplify the chirality. Such chiral environments could be achieved in the form of guest molecules or the medium as well: *i.e.,* the solvent nature such as polarity or viscosity sometimes helps to acquire a definite orientation.[3] The local guidances play an important role in supramolecular structure formation.[4] Using chiral auxiliaries[5], for example, the controlled induction of helix-sense in the aromatic moieties can bias the possibility of molecular devices, chiroptical switches, memory elements for information storage, chiral catalyses, conductive materials, etc.[6]

The π-systems, by virtue of their delocalized π-electrons, have inherent electronic properties[7] which have been utilized by the researcher in developing useful sensory systems. For the π-conjugated chromophores,[8] a long term challenge in the supramolecular chemistry is to control the local stacking arrangements which, in turn, greatly affect the physical properties of dye molecules. In this regards, perylene bisimide (PBI) dyes receive a great deal of attention owing to have numerous functionalities and potential applications.[9] Recently, Wu *et al.* reported[2h] about enantiopurity determination and differentiation of the *α*-hydroxy carboxylates by using circular dichroism (CD). They made an approach with the concept of PBI aggregation caused by the guest molecules resulting in the induced circular dichroism (ICD) and further developed sensitive and interference-free *ee* determination using the change in supramolecular chirality of the helical-stacks generated from the perylene stacks. In another work, Kumar *et al.* reported[2i] a homotropic and heterotropic allosteric on-off regulation of supramolecular chirality in the PBI aromatic core using different types of achiral bio-phosphates. In our recent work,[10a-c] it was experienced that the expression of chemical structures through spontaneous formation of nanostructure at the molecular level can alternatively be regarded as a tool to translate structural information with high precision. The guanidinium-tethered oligophenylenevinylene (OPV-G) exhibits defined fluorescence responses towards the stereoisomers, *L*- and *meso*-tartarate *via* different mode of self-assembly, J- or H-type.[10a] Thus, one can regard the mode of self-assembly at the molecular level as a function to convert structural information to optical output.

Herein, we have used the general host-guest approach in developing supramolecular structure by different chiral guests, which in turn read out the structural information in the available analytical tools. Owing to their fluorescence quenching tendency during aggregation and 'not-so-interesting' absorbance change in aqueous medium, dicationic perylene bis-guanidinium (PBG) was used to read-out the molecular informations *via* induced chirality generation. In this regards, we used some of biologically important dicarboxylic acids (DA). (Scheme 1) Tartaric acid (TA) and its derivatives are among the most common dicarboxylic acids and have been widely used for the asymmetric catalysis, resolving agent, gelators, and so forth.[10d-g] Depending on the structural variance of DAs, the aggregate formation was found to be sensitively influenced by the secondary interactions. Common DAs, including TA and diacetyl tartaric acid (DATA), were unable to deliver the expected chiral induction *via* aggregate formation at the molecular level.

When it was attempted on a TA derivative, dibenzoyl tartaric acid (DBTA), we found a strong absorbance change along with characteristic ICD (Fig. 1d) for the host, PBG (5.0X10^{-5} M) in HEPES buffer solution (pH 7.4). This finding means that only ionic interaction between the head groups or stereochemical differences are not sufficient, but the substituents in the guest molecules have a major contribution to aggregate formation varying the degree of distortion in the perylene core. The simple and effective chirality sensing associated with the structural and environmental biasness to form chiral aggregates resulted in interesting photophysical properties. In this present study, we have tried to find out and correlate the origin of the induced chirality by the chiral guest molecules and have discussed the mechanism of functional supramolecular structure formation. In order to convey our interest and to make the study simple, we have concentrated only on three TA derivatives, especially on DBTA for further exploration.



Scheme 1. Chemical structures of (a) Bis(2-(guanidinium)ethylene)perylene-3,4,9,10-tetracarboxyldiimide (PBG) and (b) Tartaric acid (TA) derivatives (*D/L*).

Results and Discussion

1. Origin of the chiral orientation in PBG·DBTA(*D/L*) complexes

Hydrophobic residues in the functional molecules engage in mutual association in an aqueous system, avoiding contacting with the water molecules and finally deprive the water solubility of the molecules. PBG was designed with the cationic head groups threaded at the imide positions with a purpose to make it water-soluble as well as to let it interact with anionic guest molecules.[11] In the present system, the pendent groups attached to TA play an important role to adjust the water-solubility. In addition, both PBG and TA derivatives are well soluble in methanol. One can expect, therefore, that there is a critical water/methanol ratio where the TA derivatives transit from monomeric dispersion to aggregate. We found that a HEPES buffered water/methanol = 40:60 *v/v* mixed solvent system (10.0 mM, pH 7.4) can satisfy this requirement and subsequent experiments were mainly carried out in this mixed solvent. The TA derivatives were used in anticipation of complex formation between complementary guanidinium and carboxylate ions assisted by both ionic interactions and hydrogen-bonding interactions.[12] Also, they were expected to form equimolar complex through cationic-anionic charge neutralization, *i.e.* through ionic self-assembly (ISA) process which would bring the perylene π-cores closer enough to form cofacial dimeric structures. To realize this optically interesting aggregation mode, we first compared the binding event by using Benesi-Hildebrand equation:[13] among the TA derivatives, it was found that DBTA has the highest apparent association constant value ($K_a = 3.5X10^2\ M^{-1}$) compared to other two derivatives, TA ($0.15X10^2\ M^{-1}$) and DATA ($1.4X10^2\ M^{-1}$). Furthermore, the bicomponent complex formation ability was compared in the buffered aqueous medium at constant 1:1 molar ratio. As a result, only DBTA has come out as an efficient candidate for aggregate formation by allowing investigations at the low concentration of chiral selector ($5.0X10^{-5}$ M) and the analytes to be used in this study.[13] We checked the Job's plot experiment[13] for the PBG·DBTA(*D/L*) complexes in HEPES buffer solvent (10.0 mM, pH 7.4). The possible binding stoichiometry was confirmed to be 1:1 ratio, which finally propped up our speculation.[14]

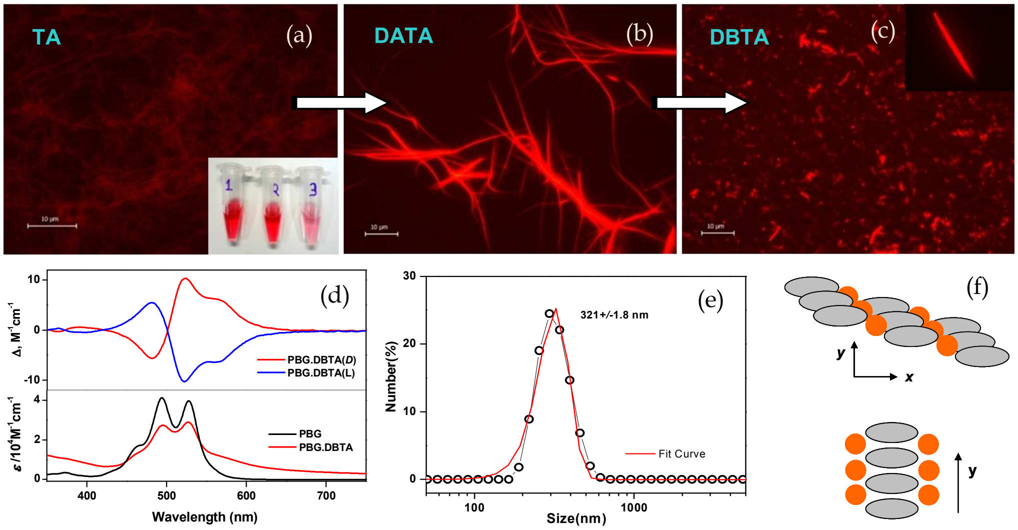


Fig. 1. (a-c) Fluorescence micrographs of the PBG·TA derivatives [*inset of Fig. (a)*: physical appearance of the complexed solutions, (1-3) denotes TA, DATA, and DBTA, respectively], (d) Absorbance (down) and ICD (up) spectra of PBG monomer and PBG·DBTA complexes (*D/L*) at $1.0X10^{-4}$ M concentration in water/methanol = 40:60 *v/v* (10.0 mM, 40:60) solvent system (pH 7.4) at 20 °C, (e) Corresponding size distribution of the PBG·DBTA aggregates measured by DLS instrument, (f) Schematic representations of the molecular arrangements depending upon the guest molecules, where the oval shapes represent the PBG monomers and the orange rounds shape represent the chiral guests. The extended (more J-type, upper) is expected for the complexes with TA and DATA, whereas the restricted (more H-type, lower) is expected for PBG·DBTA complex.

If we assume that PBG molecules form fully aggregated complex with DBTA molecules at $5.0X10^{-5}$ M concentration in this buffered aqueous solvent, then one can get information about the complex forming ability of other two TA derivatives with respect to DBTA from eqn. (1),

$$\alpha_{agg}(T) \approx \frac{A(C)-A(M)}{A(agg)-A(M)} \quad \text{……………. eqn. (1)}$$

where $\alpha_{agg}(T)$ is the mole fraction of the aggregate at temperature T, and $A(M)$, $A(C)$, and $A(agg)$ are the absorbance at 500 nm for the monomer (PBG), the complex solution of PBG with other

TA derivatives, and the PBG·DBTA aggregate solutions at temperature T, respectively.[15] Compared to DBTA, $\alpha_{agg}(T)$ values are 0.17 and 0.18 for TA and DATA complexes, respectively, indicating that the binding ability depends only on the substituents. The PBG·DBTA complex shows a decrease in the absorbance value near λ_{ex} (~500 nm, Fig. 1d), which depicts the cofacial stacking arrangement during the aggregate formation.

The bicomponent complex solutions also unveil different visual appearances. TA and DATA share the very similar complex forming affinity towards PBG (as calculated in the previous section), and both show no color change (only red, *inset*: Fig. 1a) compared to monomer solution. On the other hand, DBTA shows instant fading in color. The optical change causes spectral broadening in the absorbance study, and is briefly explained in the later part of this manuscript. The desired morphology check was studied under a fluorescence microscope (FM). It was found that the PBG·DBTA complex shows small particles like a fibrous network uniformly distributed on the matrix (Fig. 1c). Conceivably, the complex does not form a perfectly H-type aggregate that should be entirely non-emissive: instead, the small fibers show strong red fluorescence upon irradiation. The particle size was checked under dynamic light scattering (DLS) measurement (Fig. 1e), which showed a narrow number distribution. Furthermore, we checked the morphology of TA and DATA complexes in the FM experiment, which showed a continuous change in morphology along with shortening in the fiber network. It is reasonable to consider, therefore, that the PBG·DATA complex acts as the transition between the two extremes. Following our previous experiences,[10a] TA tends to form one-dimensionally extended hydrogen bonded complex with PBG, whereas DBTA intended to form restricted H-type molecular box-like structure which is unable to extend 1D fiber structure over a long range (schematically presented in the Fig. 1f). The extended networks of PBG·TA cannot show a considerable fluorescence enhancement that could be regarded as the translation of the structural information. In contrast, PBG·DBTA forms the pseudo-molecular box like stacking in the restricted structure and can induce chirality into the cofacial perylene stacks by generating an active angle between two successive transition dipoles. Therefore, the above findings can be accompanied by concluding the special selectivity of the dicationic PBG chromophore towards benzoyl-substituted TA, and the selectivity is applicable to explicit read-out of the molecular information *via* generation of the characteristic ICD spectra for *D*- and *L*-enantiomers.

2. Correlation between ICD signal and tartaric acid absolute configuration estimated by structural calculation

In the present study, we have employed the structural calculations to investigate the cause of ICD signal from the possible PBG·DBTA dimeric structure in the aqueous medium. From the preceding results, it is reasonable to assume that PBG and DBTA form a 2+2 box-like cyclic structure. Firstly, a single vibrational PBG monomer was calculated using force field energy minimization and the dimer Hamiltonian was built up by getting the crystal structural information of different perylene derivatives.[16] Also, the most stable structure of DBTA was calculated by using the lattice parameters, in which the atomic positional informations were taken from the experimental crystal structure.[17] From the comparison of all the possible 2+2 dimeric structures, we have extracted the most likely dimeric geometry (Fig. 2a). The box-like PBG·DBTA structure exhibits the most stable conformation with lowest heat of formation value of -828.5 kcal and a resultant dipole moment of 3.7 D along with a π-π stacking distance of 3.7 Å. The transition dipole moments of the monomer units in the stacks span an angle of $\theta \approx 66^{o}$. The calculated stacking distance is longer than the standard π-stacking value (3.5 Å); however this value is supported by the wide-angle X-ray scattering of the complexes.[13] These outputs allow us to anticipate the imperfect π-stacking of the perylene cores, for which several interesting physical properties are generated. The present theoretical studies predict the dipole moment originated from the cofacial dimeric stacked box-like structure and the transition dipoles assume a positive biasness which causes the generation of axial chirality into the perylene stacks by showing an ICD signal. In the lowest energy conformation of the dimeric stacks assessed by molecular calculation; the phenyl rings of DBTA are placed at the outer sphere of the complex, and are non-coplanar with the perylene chromophores and also with each other. Due to the bulkiness and the specific orientation of the phenyl rings compared to other TA derivatives, the rotational displacement is expected to observe in the aqueous medium.

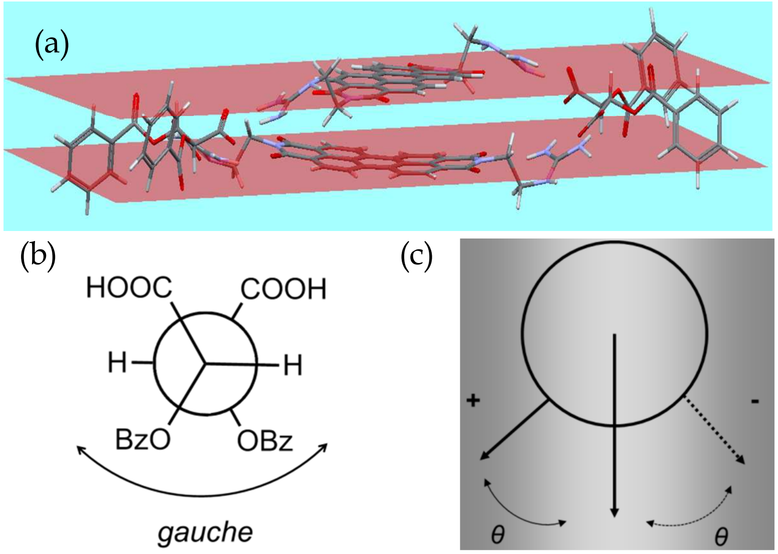


Fig. 2. Schematic presentations: (a) The most likely optimized dimeric packing structure of 2+2 PBG·DBTA complex calculated in the energy minimization process using MOPAC with PM6-DH2 Hamiltonian and COSMO method, (b) Newman projection of DBTA was derived from the obtained complex structure where the two benzoyl groups (Bz) assume *gauche* conformation, and (c) Possible displacement and generation of angle ($\theta \approx 66^{\circ}$) between the two transition dipole moments (indicated as arrow) in either directions to produce different chirality.

3. Induced circular dichroism (ICD) and chiral amplification

It is quite obvious to expect the appearance of the ICD band originated from the exciton coupling of electronic transition dipole moments of two or more neighboring perylene chromophores in the dimeric or oligomeric states.[2d,g,h,18] We found that only PBG·DBTA(*D/L*) complexes are able to show the strong ICD signals even at moderately lower concentration limit. Generation of the axial chirality into the stacked perylene chromophores was monitored in a water/methanol = 40:60 *v/v* (10.0 mM) solvent system under the apparently homogeneous condition. The spectroscopic titration using constant PBG concentration ($1.0X10^{-4}$ M) was carried out in a desire to get the information regarding how the 1:1 complex leads to form ordered oligomer structure. It is already established that the perylene-stacks tend to undergo cofacial stacking aggregation by the anionic guests, and the increased concentration induces the cofacial stacking *via* ISA. During this process, upon addition of anionic guest, the yellowish fluorescence color of PBG monomer solution was changed to reddish color,[13] which is an immense visual conformation about the higher ordered complex formation of the perylene derivatives *via* cofacial perylene-stacks formation. Both *D*- and *L*-enantiomers show significant Cotton effect with the opposite sign in the absorbance region of PBG and the bisignated CD spectra of both enantiomers create an isobestic point at 500 nm, exactly matched with the absorbance value of PBG·DBTA(*D/L*) complexes (Fig. 1d). The positive/negative signs in the Cotton effect suggest that the right/left-handed helical superstructures (*P*/*M*) were formed in the solution. The typical exciton-coupled CD signal[19] for *D*-enantiomer shows a positive amplitude at 523 nm with a $\Delta\varepsilon$ value of +10.4 $M^{-1}cm^{-1}$ followed by negative amplitude at shorter wavelength (481 nm) with a $\Delta\varepsilon$ value of -5.6 $M^{-1}cm^{-1}$, whereas for *L*-enantiomers, $\Delta\varepsilon$ values are -10.4 and +5.5 $M^{-1}cm^{-1}$, respectively. The *D* and *L* chiral auxiliaries induced the chiral sense into the perylene-stacks according to their chiral biasness by arranging the transition dipole moments.

Although the shape and sign of the ICD spectrum of *D*-complex is almost similar to that of *L*-complex, the induced handedness is not always equal in amplitude values, which may refer to experimental limits. For example, as the concentration of the anionic guest was increased, the ICD signal intensity was also increased (Fig. 3a). These results indicate that the helical sense, *P*- or *M*-type, starts to develop from the 1:1 complexed nucleation point, which is further amused in the presence of higher amount of the guest and finally form the helical oligomeric supramolecular structure.[20] Intensity of the axial chirality induced by *D*- and *L*-enantiomers with the identical *P*- and *M*-spectra can be described by eqn. 2,

$$\Delta\varepsilon \approx \pm\frac{\pi}{4\lambda}\mu_a\mu_d R_{da}^{-2}\sin(2\theta) \quad \text{.................eqn. (2)}$$

where μ_d and μ_a are the electronic transition dipole moments of the cofacially stacked two perylene chromophores, R_{da} is the center-to-center distance between two perylene-stacks, and θ is the angle between transition dipoles.[21] The sin(2θ) dependence results in the zero intensity when $\theta = 0$, 90, or 180$^{\text{o}}$ and the maximum intensity when $\theta = 45$ or 135$^{\text{o}}$. The gradual decrease in the signal intensity against temperature and concentration for the PBG·DBTA complex is assignable to the loses of the oligomeric structures,[13] and even the very low intensity is consistent with the dimeric state perpendicular to the PBG long axis, the preferred geometry for the unconstrained dimers and aggregates. This trend is in accordance with the previously discussed molecular modeling where the calculated dimeric structure keeps an angle of about 66$^{\text{o}}$ between two dipoles with the resultant dipole moment of 3.7 D.

In addition, a highly efficient chiral amplification was observed during the ICD titration as a function of the enantiomeric excess (*ee*) of the chiral guest. The induced helical sense was found to exhibit a sigmoidal change in the *ee* plot (Fig. 3b) by subsequent addition of the chiral guest molecule. This experiment implies that addition of one enantiomer into the PBG solution generates the nucleation point of the 1:1 complex with the selective helical sense, which is further amplified by the cooperative chiral interaction with the host molecule. Here, the modified 'sergeants-and-soldiers'[2f,6b,22] is experienced, where the first chiral guest produces the chiral units (the 'sergeants') and the next guest controls the amplification, *i.e.,* performs as the 'soldier'. The much larger CD intensity in the *ee* experiment is an indicative of a non-aligned aggregate formation. The controlled enhancement in the signal intensity in the presence of next chiral guest enantiomer can be correlated with the 'symmetry breaking law'[23], and our observations provide a scenario for the hypothesis that the deterministic evolution of the biological handedness could be possible in a precise manner in a supramolecular system.

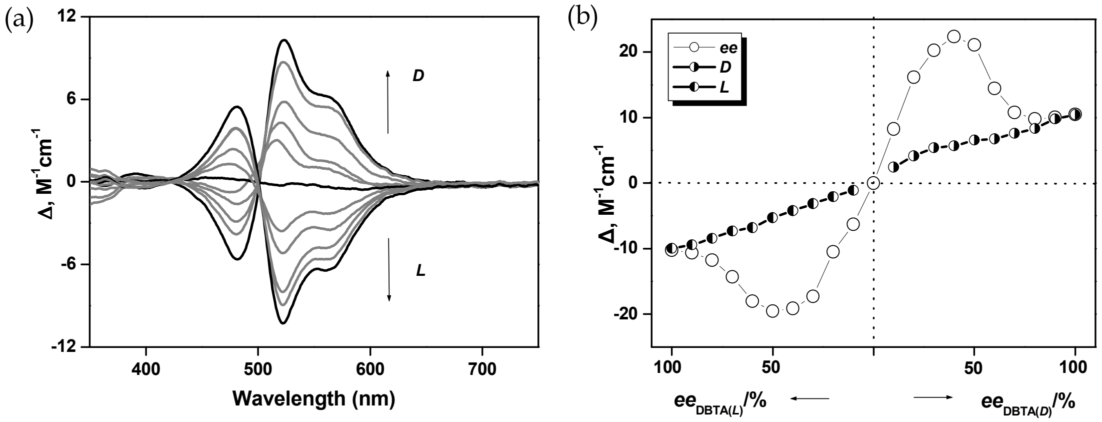


Fig. 3. (a) Spectroscopic titration of ICD signals with the changing concentration of DBTA (up to 3.0 mM) against a constant concentration of 1.0X10^{-4} M PBG, (b) Plots of ICD intensity change (at 520 nm) of PBG mediated by DBTA of varying *ee* value in water/methanol = 40:60 *v/v* (10.0 mM, 40:60) solvent system (pH 7.4) at 20 °C. The complexes were formed by subsequent addition of DBTA-enantiomers (total concentration of 3.0 mM) into the 1.0X10^{-4} M PBG solution.

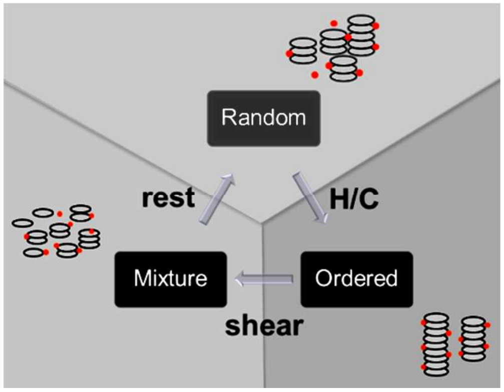
The ICD profiles for the complexes, which were produced in simple mixing followed by heating-cooling procedure in HEPES buffer, have similar biasness with the difference in spectral structure and in intensities which is comprised of an important information about the growth mechanism.[13] Indeed, it supports our initial conflict on the spectral differences based on the synthetic procedure. After having information on the selectivity of DBTA over other TA derivatives, in a deterministic way, we can now obtain the more likely image for the structure formation between PBG and DBTA, and further we have tried to build up functional outputs.

4. Diversity in aggregation of PBG·DBTA complex depending on the preparation method (particularly, related to Mixing *vs*. Heating-Cooling)

The complex formation was performed in both simple mixing (Mix) and heating-cooling (H/C) method in a buffered aqueous medium. We found, however, that the H/C method produced more organized self–assembled complex, which is evidenced by the more developed optical spectra[13]. The PBG·DBTA(*D/L*) complex prepared in the Mix method showed a change in absorbance and ICD spectra along with quenching in the fluorescence intensity. On the other hand, the H/C method produced complexes with developed and symmetrical ICD spectra and also showed the larger change in the absorbance spectra of *D*- and *L*-enantiomers. The complexes exhibited fluorescence enhancement compared to PBG at the same conditions, which is specific to the organized complex structure formation.

In general, perylene dyes exhibit the largest intermolecular interaction energy among all dyes, which is further enhanced in water by a pronounced hydrophobic effect. Interruption of the extended hydrogen bonding network of water leads to the appearance of the large π-conjugated dye molecules and the interplay between thermodynamic parameters causes the clustering of these hydrophobic objects in water.[24] Although the cationic head-groups were used to make PBG as water soluble, it shows dynamic equilibrium (at $5.0X10^{-5}$ M) between monomer and dimer or oligomer in an aqueous medium.[11] When the dianionic DBTA was added to form complex with PBG by simple mixing, the partially aggregated PBG molecules directly form supramolecular complexes *via* ISA. This tentative self-assembled structure produces a large number of quenching sites along the direction of structure formation.[25] In contrast, the complex formed in

H/C method shows fluorescence enhancement which is quite unexpected to the perylene chemistry (Fig. 5b).



Inputs / Outputs	Mix	H/C	S
PL	✗	✓	✓
ICD	✓	✓	✗

Fig. 4. (left) Schematic representation of the different states of PBG·DBTA complex prepared in different methods; (right) Correlation table was built-up with the PL and ICD intensities as the outputs in the presence of different stimuli.

The diversity in physical properties of the self-assembled PBG·DBTA complexes can be correlated with applying stimuli, like H/C or shear as sonication. To summarize possible correlations, we have taken the opportunity to draw a table along with the outputs in PL and ICD intensities (Fig. 4). It was already discussed that the H/C method shows different physical outputs compared to the Mix method. In addition, application of shear on the H/C complexes caused dissociation of the well-developed oligomer structures leading to decrease in the CD intensity. During the application of shear, the dissociated structure generates monomers and even more in a number of dimer/small-oligomer units, which cause the enhancement in fluorescence intensity. Interestingly, when this sheared solution was left in rest for a while (up to 1 hr), the dissociated complexes reunite to form the structure which has the physical properties parallel to the complexes produced in the Mix method.[13] Therefore, this shear induced regeneration of the initial state can be experienced in a periodic way by the application of stimuli.

5. Spectral change arising from π-stacking

Several interesting phenomena can arise during 'restricted stacking'[26]. of dye molecules that contain a fully planar π-system. Referenced from the previous examples, one of such phenomena is the packing of the substituents on the imide nitrogen of PBI unit that control the mode of one dimensional aggregation in solution.[8e,15,24,18] It is quite interesting to see the effect of chromophoric interactions at the outer sphere of the perylene core: in addition, in a bicomponent interaction system the substituents on the guest components have an important role in the packing restriction. This secondary effect has suddenly become the important factor in the directed self-assembly by changing the spectral properties of the principal chromophoric unit.

In the present study, the investigation was commenced on by measuring optical changes caused by the PBG·DBTA(*D/L*) aggregate formation (Fig. 5) . The absorbance data at $5.0X10^{-5}$ M show the usual broadening of the spectra for both *D*- and *L*-complexes, which is apparently caused by the adaptation of herringbone packing or slipped cofacial configuration by the perylene core units.[27a] The π-HOMO to π*-LUMO electronic transitions of PBG in an aqueous medium is not well isolated from the other allowed transitions. The electronic absorption spectrum of the monomer shows the highest Franck-Condon progression (F-C) factor for $A^{0\rightarrow1}$ with the significant decrease in the F-C value ($A^{0\rightarrow0}/ A^{0\rightarrow1}$). The dynamic aggregation behavior of the perylene-stacks was channelized into well-ordered static structure formation, shuffled by the heating-cooling process in the presence of diacids. In the aggregates, the molecular dipole moments of perylene dyes get well arranged and the relative absorption favors 0→1, 0→2 or higher transitions. These results indicate the better vibronic wave function overlap between $<\chi_{v'}|\chi_{v0}>$ (where, v'>0), which is an outcome of the PBG·DBTA self-assembled structure.[27a,b]

Consequently, in the emission process, the vibronic overlap integral $<\chi_{0'}|\chi_{v}>$ favors the relative transition to the higher vibronic ground state (v=0,1,2,3). Thereby, the emission at higher wavelength becomes intensified and the emission color becomes redder. The energy difference between two successive transitions in the emission spectra was calculated [$\Delta E=hc(1/\lambda_1-1/\lambda_2)$, *hc* =1241.5 eV·nm] at two different concentrations for the equimolar complexes. The energy difference was found to increase from 0.16 eV at $5.0\text{X}10^{-5}$ M to 0.26 eV at $2.5\text{X}10^{-4}$ M, which is in accordance with the absorption spectra. This increase in ΔE values signifies the transition to the higher vibrational ground state (v= 1,2,3). In addition, the emission spectra have an additional broad peak appearing at higher wavelength. The higher wavelength peak intensity gradually increases with respect to the original emission intensity as the concentration is increased. Formation of the excited-state dimer in the π-π aggregates was beautifully narrated by Würthner *et al.*[28c] The photoexcitation process enables molecules to excite between the stacks in the aggregates, and during the relaxation process, the π-π distance is reduced in comparison to the ground state. This leads to generation of higher vibrational energy on the ground state potential surface. Despite of the similarities, the cofacial π-π stacking interaction in one-dimensional stack creates rotational displacement between the perylene chromophores. The electron deficient imide groups embedded in the electron rich central perylene unit, and in this symmetry breaking process, it is more likely to experience some charge-transfer property in the aggregated excited state.

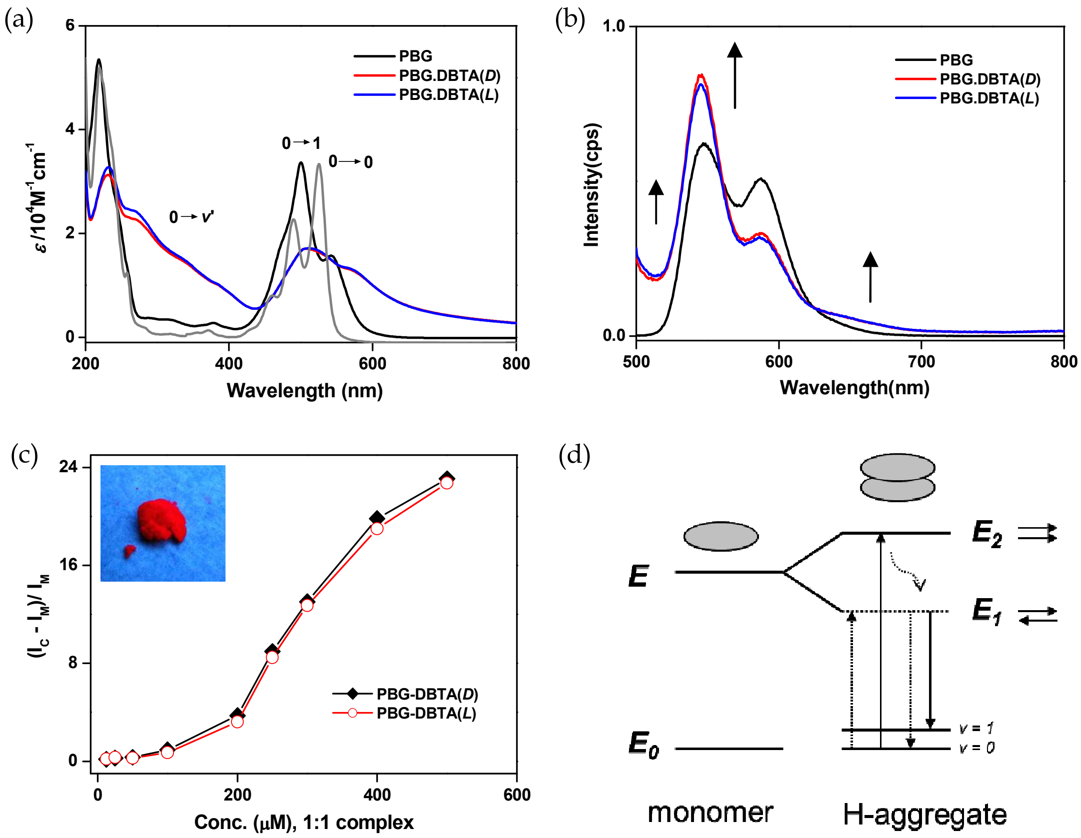


Fig. 5. Self-assemble PBG·DBTA(*D/L*) complexes were prepared at 1:1 mole ratio and 5.0X10^{-5} M concentration by H/C method in HEPES buffer solution (10.0 mM, pH 7.4) at 20 ^{o}C: (a) UV-vis spectra of PBG monomer in water (black), in methanol (gray), and the D/L-complexes & (b) the corresponding Photoluminescence (PL) spectra excited at 480 nm (c) Relative enhancement of fluorescence Intensity of the complexes (I_C) w.r.t. monomer emission(I_M) against the complex concentrations (1.25X10^{-5} to 5.0X10^{-4} M) (d) Schematic diagram: The oval shaped disk was used to designate the perylene unit. H-Stacking of the monomers results in an energy levels split between parallel and anti-parallel dipole orientations. Most of the oscillator strength of the coupled dimeric system is transferred to the higher-energy transition. Relaxation in the excited-state manifold necessitates emission from the lower-energy level, which is only weakly coupled to the ground state.

Therefore, the excimer and charge transfer interaction carry some contribution to the observed red color and higher peak generation in the emission spectra.[28] Generation of the excited stacks of perylene units could be possible from the coupled molecular vibration arising from resonance of molecular (Frankel) and charge transfer state. However, the aggregation-induced enhancement of the emission (AIEE) and the formation of excimer-type broad peak at higher wavelength were exhibited in an equal extent by both optical enantiomers of DBTA (Fig. 5c). The enhancement of the AIEE peak intensity with respect to the monomer was monitored against the concentration of the PBG·DBTA (*D/L*) complexes: it was confirmed that the relative intensity follows a sigmoidal growth which, in turn, supports that the AIEE is directly an outcome of the ordered oligomeric structure formation.

5.a. Solid state emission

The relative fluorescence enhancement (AIEE) could be effective in fabrication of supramolecular fluorescent solid-state materials (*inset*: Fig. 5c). To evaluate this idea, we prepared a high concentrated solution ($2.5X10^{-4}$ M) of 1:1 complex by the H/C method and lyophilized it in the fridge-dryer. The solid material, inherently built-up with maintaining the supramolecular structure, was able to show an intense fluorescent red light under illumination (at 365nm). Thus, the non-covalently fabricated supramolecular complexes can provide an easy and efficient way to generate highly fluorescent supramolecular solid-state materials that should be originally non-emissive owing to concentration quenching. In contrast, the Mix method was unable to produce such solid fluorescent material. The difference in the packing pattern in the complexes is the reason for this discrepancy.[13] Although the difference in axial chirality generated by the difference in chirality of the guest chiral stimulator (DBTA(*D/L*)) could not allow to experience the different level of fluorescence output, one could try to find some suitable chiral guest that may fulfill the expectations, depending on the preparation methods.

Conclusions

In summary, we have presented here a novel approach to understand the molecular recognition processes initiated by the structural differences in the guest molecules. The structural differences lead to form stable nano-structure at the molecular level, which can be alternatively regarded as a tool to translate structural information into an output in the useful analytical tools with high precision. Based on the substituent as a chiral auxiliary in the tartaric acid, the hydrophobic interaction could play as the local guidance, which further induces chirality in the nano-structure by guiding the stacking pattern of the perylene molecules. The dicationic perylene can recognize only the dibenzoyl tartaric acid derivatives among the others. The induction of chirality into the perylene stacks can also be affected by the absolute configuration of the chiral guests. In the *ee* experiment, consecutive addition of the enantiomers caused ‘symmetric breaking’ in the growth process resulting in the chiral amplification. This special selectivity inducing chirality is correlated with the molecular modeling and spectroscopic investigations. The outputs perhaps anticipate the imperfect π-stacking in the lowest energy conformation of the H-type 1:1 dimeric stack with relatively higher stacking distance (3.7 Å) and positive dipolemonent (3.67 D), along with a chiral biasness. The extended photophysical properties are established and correlated with the dependency on the chiral guests as well as on the complex formation procedures. The free interactions between host and guest lead to develop well-ordered packing structure resulting in fluorescence enhancement in solution as well as in solid state, which could be used to develop functional fluorescent materials. We thus believe that in a predeterministic way, the molecular recognition stands for the initial crosscheck to develop functional supramolecular structure.

Experimental section:

Materials:

Bis(2-(guanidinium)ethylene)perylene-3,4,9,10-tetracarboxyldiimide (PBG) was synthesized by following the procedure reported by our group.[11] All the commercially available Tartaric acid derivatives and Methanol were purchased from Wako Pure Chemical, Ltd.. 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) was obtained from Sigma-Aldrich chem. co.. Water was purified with a Direct-Q system (Millipore, Co.). The 10mM HEPES buffer solution of pH 7.4 (at 25 ^{o}C) was prepared by following literature available. We carefully monitored all the complex solutions (1:1 ratio) on desk at normal room temperature, and found good stability of the solutions over a month.

Techniques:

(i) Absorption spectra were recorded on a JASCO V-670 quipped with a peltier-type thermostatic cell holder using a quartz cell with 1 mm path length, (ii) Fluorescence spectra were recorded by Perkin-Elmer LS55 luminescence spectrophotometer at room temperature (20 °C) using quartz cells with 1 mm path lengths and excitation wavelength is of 480nm, (iii) Induced Circular dichroism spectra were recorded on a JASCO J-720-WI spectrophotometer using water jacketed cylindrical quartz cell with 0.5 cm path length, (iv) DLS measurements were conducted on the Malvern Zeta sizer Nano-ZS, (v) Fluorescence images of the cuvette containing sample solutions were snapped with a digital camera, irradiated under the UV lamp of 365 nm wavelength, (vi) Fluorescence microscopy images were observed in DM2500 microscopy (Leica) with N2,1 (*ex.* 515-560 nm and *em.* >580 nm). One drop of the PBG·DBTA complex solution was sandwiched between cover glasses and fixed by adhesive, (vii) XRD analysis was conducted on a RIGAKU smart-lab with a copper K-alpha source, and the samples were prepared by fridge-drying method and (viii) To calculate complex structure SCIGRESS MO Compact V1 Pro (Fujitsu) was employed. The detail method can be found in the latter section of the supporting information.

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Keywords: Molecular recognition, Tartaric acid, Chiral induction, Self-assembly, Aggregation enhanced emission.

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