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Two-phase Couette flow linear dichroism measurement of the shear-forced orientation of a palladium(II)-induced aggregate of thioether-derivatised subphthalocyanines at the toluene/glycerol interface

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Formation of the Pd(II)-induced thioether-derivatised subphthalocyanine **Subpc(SR)$_6$** (R = Et (ethyl) or Bz (benzyl)) aggregate at the toluene/glycerol interface was investigated by means of a new *in situ* spectrophotometric method using two-phase Couette flow (TPCF). The shear-forced orientation of the aggregate of **Subpc(SR)$_6$**–Pd(II) complexes formed at the toluene/glycerol interface was studied by their linear dichroism (LD) spectra. The H-aggregate of the **Subpc(SEt)$_6$**–Pd(II) complex gave no LD signal, but the J-aggregate of the **Subpc(SBz)$_6$**–Pd(II) complex clearly afforded LD spectra at a wide range of rotation speeds, suggesting a longer J-aggregate structure in the **Subpc(SBz)$_6$**–Pd(II) system. The relaxation kinetics of the shear-forced orientation of the Pd(II)–**Subpc(SBz)$_6$** aggregate were observed after stopping the rotation and analysing using a multi-exponential decay equation. By increasing the **Subpc(SBz)$_6$** concentration in toluene, the fast relaxation fraction of 6.6–7.5 seconds decreased and the slow relaxation fraction of 292–322 seconds increased. The results obtained in this study demonstrate that the TPCF method is useful for studying the size distribution of aggregates formed at liquid/liquid interfaces.

Introduction

The aggregates of functional molecules or the large assemblies of interacting pigments are interesting systems, since they exhibit characteristic structural and electronic properties. For example, the chlorosomes (light-harvesting antennae of green photosynthetic bacteria) are constructed from aggregated bacteriochlorophyll c molecules.[1–3] As the closest counterpart to porphyrin (Pr), phthalocyanine (Pc) and its related compounds are also of interest for understanding the properties of long-wavelength pigments for light-harvesting systems, photodynamic therapy (PDT) and non-linear optics.[4,5] The arrangement of functional dye assemblies has been focused-on recently as a new methodology for nanocomposites, nanowires and nanocircuits,[6–10] which are indispensable in nanotechnology. In our previous work, we have reported the well-defined and rigid Pd(II)-induced aggregate of thioether-derivatised subphthalocyanine **Subpc(SR)$_6$** (R = Et (ethyl) or Bz (benyl), see Fig. 1) by using a liquid/liquid interface as a two-dimensional flat template.[11]

The liquid/liquid interface that exists between an organic phase and an aqueous phase can be adsorbed by any solvophobic or amphipathic molecules from the organic and aqueous phases. At the liquid/liquid interface, it is expected that aggregates that are not formed in bulk phase can be formed easily,[12–14] because the intermolecular distance between adsorbed monomers becomes much shorter than in bulk phase, even at a very low bulk concentration. Nowadays, the liquid/liquid interface is recognized to be a novel two-dimensional reaction field for the separation and detection of molecules.[15,16]

Measuring linear dichroism (LD) to study the spectroscopic properties and structure of orientable, light-absorbing molecules in solution is well established, but, as far as we know, never at liquid/liquid interfaces. The flow-orientation method has been extensively used, for example, in the study of micron-size nucleic acids.[17,18] In the present study, the aggregates of **Subpc(SR)$_6$**–Pd(II) complexes formed at the toluene/glycerol interface have been studied by a novel *in situ* two-phase Couette flow (TPCF) technique that can provide hydrodynamic as well as spectroscopic information about the structure of aggregates at the interface. In the TPCF method, shear-flow forces are sufficient to induce a highly oriented interfacial aggregate of **Subpc(SBz)$_6$**–Pd(II) complexes. Furthermore, stopped-flow relaxation kinetic studies have given unique time-resolved information on the interaction between and organization of the aggregates formed at the toluene/glycerol interface.

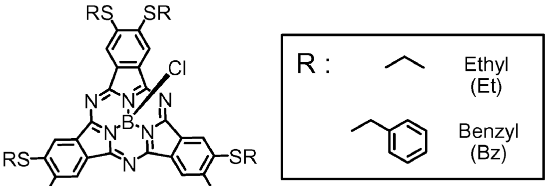

Fig. 1 Molecular structure of thio-derivatised subphthalocyanine compounds (**Subpc(SR)$_6$**).

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Table 1 UV-vis spectral parameters of thioether-substituted subphthalocyanine in toluene[a]

Compound	λ_{max}/nm (log ε/M^{-1} cm^{-1})			
Subpc(SEt)$_6$	592 (4.77)	546 (sh)	362 (4.14)	296 (4.55)
Subpc(SBz)$_6$	601 (4.78)	555 (sh)	386 (4.21)	304 (4.52)

[a] sh = shoulder.

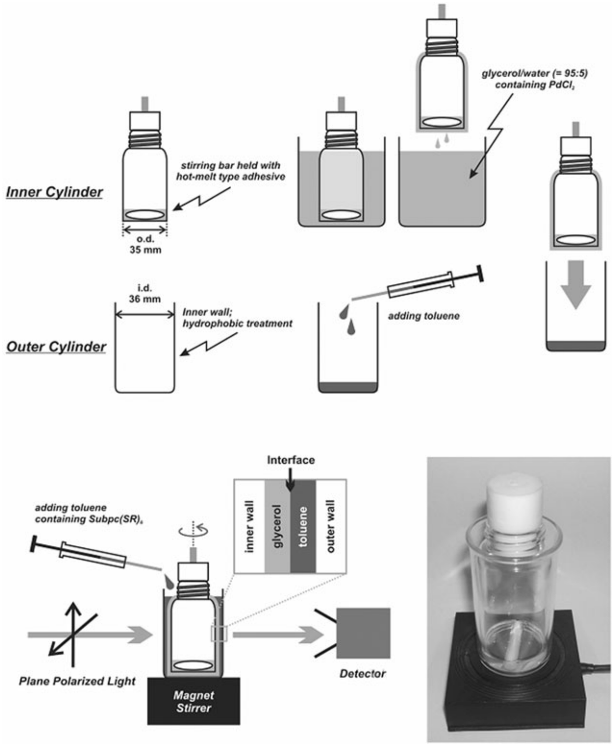
Experimental

Materials

Toluene and glycerol were purchased from Nacalai Tesque Inc. (Kyoto, Japan). Water was distilled and de-ionized by a Milli-Q system (Millipore, USA). Subphthalocyanine derivatives with six thioether groups at the peripheral benzene site (**Subpc(SR)$_6$**; R = Et (ethyl) or Bz (benzyl)) were prepared as described previously.[11] UV-vis spectral data of **Subpc(SEt)$_6$** and **Subpc(SBz)$_6$** are listed in Table 1. All other chemicals were of reagent grade from Wako Pure Chemicals (Osaka, Japan), and were used as received without further purification.

UV-vis absorption and linear dichroism spectra measurement in two-phase couette flow system

To measure UV-vis absorption and LD spectra, the aggregates of the **Subpc(SR)$_6$**–Pd(II) complexes were formed at the toluene/glycerol interface under a shear-flow force in a two-phase Couette flow cell. Scheme 1 shows a schematic drawing of the two-phase Couette flow cell (TPCF cell), which consists of two concentric glass cylinders, a stationary outer cylinder, a rotating (100–800 rpm) inner cylinder and a magnetic stirrer. The inside diameter of the outer cylinder is 36 mm, while the outside diameter of the inner cylinder is 35 mm; thus, the annular gap is 0.5 mm and the total optical path length in the TPCF cell is 1.0 mm. The inner wall of the stationary outer cylinder was treated with dichlorodimethylsilane in toluene to give a hydrophobic coating so as to make a stable toluene/glycerol interface. A PTFE magnetic stir bar was attached to the bottom of the inner cylinder using a hotmelt-type adhesive (MORESCO melt S-1979, MORESCO, Japan) and rotated by a magnetic stirrer.



Scheme 1 Sample preparation scheme for the thin two-phase toluene/glycerol, and the interfacial aggregate of **Subpc(SR)$_6$**–Pd(II) complexes prepared for UV-vis absorption and LD measurement using a two-phase Couette flow (TPCF) cell.

The degree of alignment of the interfacial aggregate of **Subpc(SR)$_6$**–Pd(II) complexes is probed using polarized light that is oriented at a 90° angle with respect to the axis of rotation; the absorbance measured by the polarized light parallel and perpendicular to the rotation axis are designated by $A_{//}$ and $A_{\perp}$, respectively. The LD signal is defined as the difference between the two absorbances:

$$\mathrm{LD} = A_{//} - A_{\perp} \qquad (1)$$

The probing light beam enters the TPCF cell radially, as shown in Scheme 1; the horizontally-polarized light is thus parallel to the flow direction and the vertically-polarized light perpendicular to it.

The toluene/glycerol interface in the TPCF cell for UV-vis absorption and LD measurements was prepared using the following procedural steps: (i) The inside cylinder was dipped into the glycerol solution containing $PdCl_2$ aqueous solution (5% volume). (ii) The toluene (2 mL) was added into the outside cylinder. (iii) The inside cylinder, where the glycerol solution adhered to outside wall with *ca.* 0.25 mm thickness, was inserted into the outside cylinder. (iv) A blank spectrum was measured with the inside cylinder rotating at an appropriate velocity. (v) After the toluene solution (1 mL) containing **Subpc(SR)$_6$** was put into the TPCF cell using a microsyringe (Hamilton, USA), it was rotated again for a few minutes until the highly-ordered orientated aggregate of the **Subpc(SR)$_6$**–Pd(II) complex was formed at the toluene/glycerol interface in the TPCF cell. (vi) The UV-vis and LD spectra through the bulk phases and the interface were recorded on a 8453 (Agilent, USA) spectrometer and a J-810 (JASCO, Japan) spectropolarimeter, respectively. Polarized light spectra were averaged over several scans when necessary. It is well-known that Taylor instability (turbulent flow) between two phases would yield microscopic droplets of one solvent in the other, and then that elliptically-shaped droplets would give rise to light scattering LD (especially in the shorter wavelength region).[19–21] However, in the present experiment (<500 rpm), such linear dichroism was not observed. Moreover, after stopping the rotation, the stable toluene/glycerol interface in the TPCF cell could also be kept for at least 1 h.

Other apparatus

The viscosity measurements were performed on a Viscometer B8H (TOKIMEC, Japan). The concentration of palladium ion was determined using a polarized Zeeman atomic absorption spectrophotometer Z-5310 (Hitachi, Japan) equipped with a hollow cathode lamp L233–46NQ (Hamamatsu Photonics, Japan).

Unless specified, all measurements in this study were carried out in a thermostated room at 25 ± 2 °C.

Results and discussion

UV-vis absorption spectra of Subpc(SR)$_6$–Pd(II) aggregates in the toluene/glycerol system using a TPCF cell

Aggregation of **Subpc(SR)$_6$** with Pd(II) at the toluene/glycerol interface induced changes in the UV-vis absorption spectrum in the Q band region. The extent of the blue- or red-shift depends on the interaction mode between **Subpc(SR)$_6$** molecules.[22,23] Generally, the blue-shift is ascribable to a repulsive electrostatic interaction and the red-shift to an attractive electrostatic interaction. From a preliminary determination of the palladium ions in the toluene phase and **Subpc(SR)$_6$** compounds in the glycerol phase by atomic absorption and UV-vis absorption spectrometry, respectively, after shaking the toluene and glycerol phases, it was confirmed that Pd(II) ions were not extracted with **Subpc(SR)$_6$** from the glycerol phase to the toluene phase, and **Subpc(SR)$_6$** compounds in the toluene phase were not distributed into the glycerol phase. UV-vis absorption spectra of the aggregates of **Subpc(SEt)$_6$**–Pd(II) and **Subpc(SBz)$_6$**–Pd(II) complexes formed at the toluene/glycerol interface are depicted in Fig. 2(a) and Fig. 2(c), respectively, upon increasing the amount of Pd(II) in the glycerol phase. For comparison, the UV-vis absorption spectra of the aggregates of **Subpc(SEt)$_6$**–Pd(II) and **Subpc(SBz)$_6$**–Pd(II) complexes formed at a toluene/water interface are also shown (Fig. 2(b) and Fig 2(d), respectively).[11] The interfacial aggregate of **Subpc(SEt)$_6$** exhibited a blue-shifted maximum at 545 nm compared to that of the monomer in toluene. On the other hand, in the case of **Subpc(SBz)$_6$**–Pd(II) system, a red-shift in the Q band region (the maximum at 629 nm) was observed. Although the maximum and shape of the interfacial aggregate in the toluene/glycerol system are slightly different, these results are thought to be almost the same as those observed in the toluene/water system, suggesting that, at the toluene/glycerol interface, **Subpc(SEt)$_6$** and **Subpc(SBz)$_6$** also form H-aggregates (face-to-face type) and J-aggregates (end-to-end type), respectively, bound with Pd(II). The inverted shifts between **Subpc(SEt)$_6$** (blue-shifted) and **Subpc(SBz)$_6$** (red-shifted) will be explained by the geometry of **Subpc(SR)$_6$** compounds and their aggregates being adsorbed at toluene/glycerol interface.[11]

Unidirectional formation of aggregates of Subpc(SBz)$_6$–Pd(II) complexes at the toluene/glycerol interface under shear-flow conditions

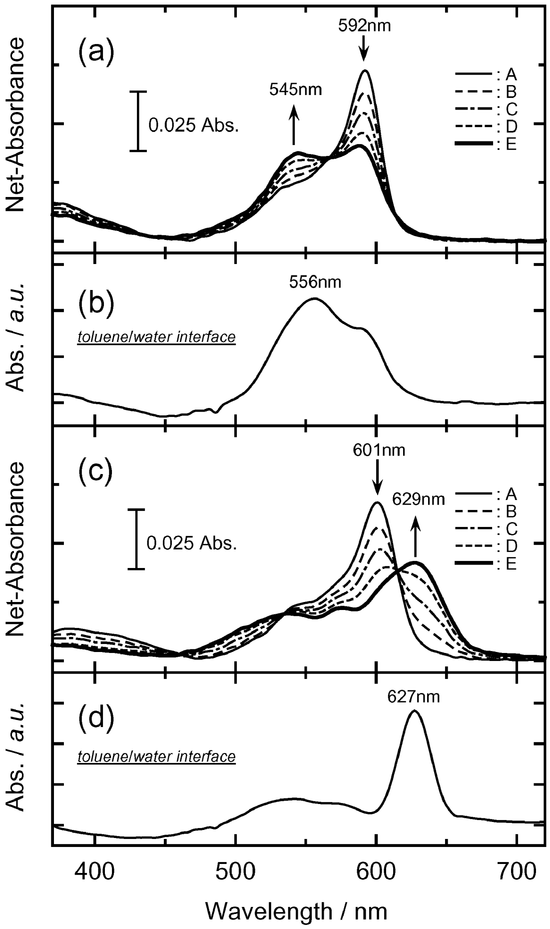


Fig. 2 Changes to the TPCF absorption spectra of (a) **Subpc(SEt)$_6$** and (c) **Subpc(SBz)$_6$** in the toluene/glycerol system following the addition of various PdCl$_2$ concentrations of (A) 0 M, (B) 1.0 × 10^{-5} M, (C) 3.0 × 10^{-5} M, (D) 1.0 × 10^{-4} M and (E) 5.0 × 10^{-4} M. [**Subpc(SR)$_6$**] = 3.0 × 10^{-5} M. Absorption spectra for (b) **Subpc(SEt)$_6$**–Pd(II) and (d) **Subpc(SBz)$_6$**–Pd(II) in a toluene/water system (from ref. 11) [Reproduced with permission from *Soft Matter*, 2005, **1**, 292–302. Copyright 2005 Royal Society of Chemistry]. The arrows indicate the direction of the absorbance changes as the Pd(II) concentration was increased. Rotation speed = 500 rpm.

Fig. 3(a) and Fig. 3(b) depict the measured LD spectra for the **Subpc(SEt)$_6$**–Pd(II) and **Subpc(SBz)$_6$**–Pd(II) systems, respectively. **Subpc(SBz)$_6$** exhibits a positive LD signal in the J-aggregate absorption region. It is suggested that the aggregate of **Subpc(SBz)$_6$**–Pd(II) complexes formed at the toluene/glycerol interface has an anisotropic shape and that the main J-aggregate transition of **Subpc(SBz)$_6$**–Pd(II) complexes is oriented preferentially along the flow direction. Unlike the **Subpc(SBz)$_6$**–Pd(II) system, we could not observe any LD signals in **Subpc(SEt)$_6$**–Pd(II) system, indicating that the aggregates of **Subpc(SEt)$_6$**–Pd(II) complexes formed at the toluene/glycerol interface could not be oriented by the flow. The transition dipole of **Subpc(SEt)$_6$**–Pd(II) complexes in the H-aggregate formed at the toluene/glycerol interface seems not to be oriented like **Subpc(SBz)$_6$**–Pd(II) complexes in the J-aggregate.

As shown in Fig. 4, the LD signal of the flow-oriented interfacial aggregate of **Subpc(SBz)$_6$**–Pd(II) complexes at the steady-state of assembly is plotted against the rotational velocity in the range 50–800 rpm. Saturation was obtained at 400–500 rpm. However, a certain decrease in LD signal was found at values higher than 500 rpm. Except for a mechanical factor in the TPCF cell (such as a pulsation), this LD decrease is not only due to flow-degradation of the interfacial aggregate

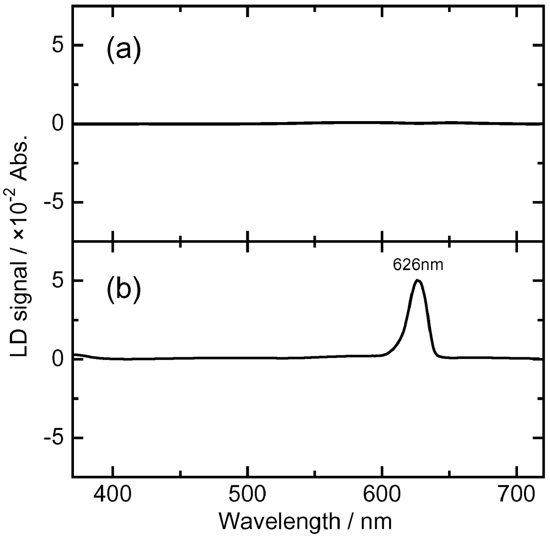


Fig. 3 LD spectra of (a) the **Subpc(SEt)$_6$**–Pd(II) system and (b) **Subpc(SBz)$_6$**–Pd(II) system in toluene/glycerol. [**Subpc(SR)$_6$**] = 3.0 × 10^{-5} M. [Pd(II)] = 5.0 × 10^{-4} M. Rotation speed = 500 rpm.

structure, but may also be explained by so-called Taylor centrifugal interface instability.[19–21]

Immediately upon stopping the rotation, a relaxation of the aggregate to a random orientation for **Subpc(SBz)$_6$**–Pd(II) complexes took place. As given in Fig. 5, for example, the relaxation curves are not single exponentials, but can be fitted to a multi-exponential decay:

$$\mathrm{LD}(t) = \sum_{i=1}^{n} P_i \cdot \exp(-t/T_i) \qquad (2)$$

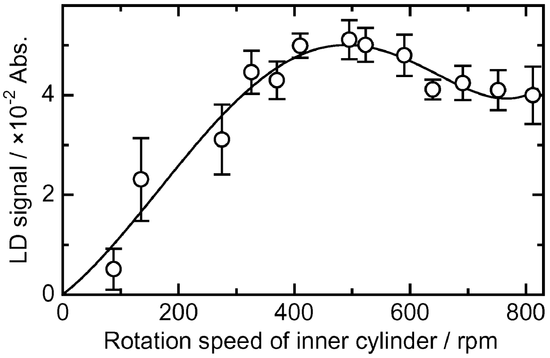


Fig. 4 LD signal at 626 nm of the aggregate of **Subpc(SBz)$_6$**–Pd(II) complexes in toluene/glycerol as a function of rotational velocity. The line provides a visual guide. [**Subpc(SBz)$_6$**] = 3.0 × 10^{-5} M. [Pd(II)] = 5.0 × 10^{-4} M.

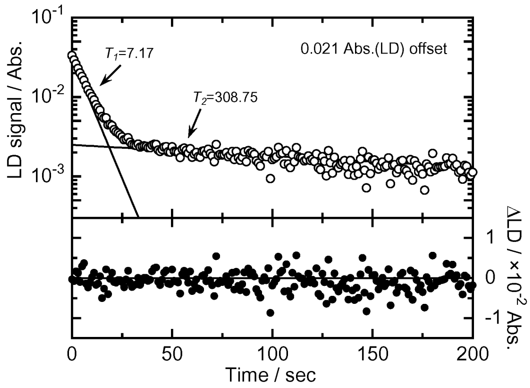


Fig. 5 Relaxation of the oriented aggregate of **Subpc(SBz)$_6$**–Pd(II) complexes formed at the toluene/glycerol interface. After orientation at 500 rpm, the rotation was stopped and the decay in the LD signal at 626 nm recorded as a function of time. The decay curve was fitted to a multi-exponential with a residual term ("offset" 0.021 Abs.) with T_i = 7.17 and 308.75 s. Below the plots is their regression error. [**Subpc(SBz)$_6$**] = 3.0 × 10^{-5} M. [Pd(II)] = 5.0 × 10^{-4} M.

LD(t) denotes the LD signal at time t. P_i is the amplitude of the pre-exponential factor and T_i is the relaxation time constant. From the analysis of the LD decay curve, time constants in the orders of about 7, 300 and above 2000 seconds were obtained for "fast" and "slow" processes, and an "offset", respectively (Table 2). The amplitudes of the pre-exponential factors P_i, reflecting the contributions from the different relaxation processes, showed different dependencies on the concentration of **Subpc(SBz)$_6$** in the toluene, suggesting some relationship between the factor and the interfacial coverage of the aggregate. The relative contribution from the "offset" term increases with increasing **Subpc(SBz)$_6$** concentration. Above 1.0 × 10^{-4} M, the relative contribution from the "offset" appears to become approximately a constant 70%, indicating the existence of a very stable interfacial aggregate, maintaining a unidirectional orientation. The relaxation behavior can be interpreted in terms of the difference in size of the aggregate or interfacial coverage of the aggregate at the interface. The two possible processes will be (a) a fast individual reorientation of each small aggregate with its rotational freedom guaranteed by a surrounding free area, and (b) a slow coupled reorientation of large aggregates due to their mutual interaction. The "fast" component (T_1 = *ca.* 7 s) seems to be predominant at lower **Subpc(SBz)$_6$** concentrations. For the "slow" component (T_2 = *ca.* 300 s) shown in Table 1, higher **Subpc(SBz)$_6$** concentrations stabilize extended interfacial aggregates. The concentration dependence of the "fast" and "slow" components seem to be consistent with considerable entanglement between the aggregates of **Subpc(SBz)$_6$**–Pd(II) complexes. The observed T_i value can be related to the aggregate length (L) and diameter (d) of a rigid rod by Broersma's relationship[24,25]

$$\Theta = \frac{3kT}{\pi\eta L^3}F \qquad (3)$$

Table 2 Shear-flow orientation relaxation of the interfacial aggregate of **Subpc(SBz)$_6$**–Pd(II) complexes by LD

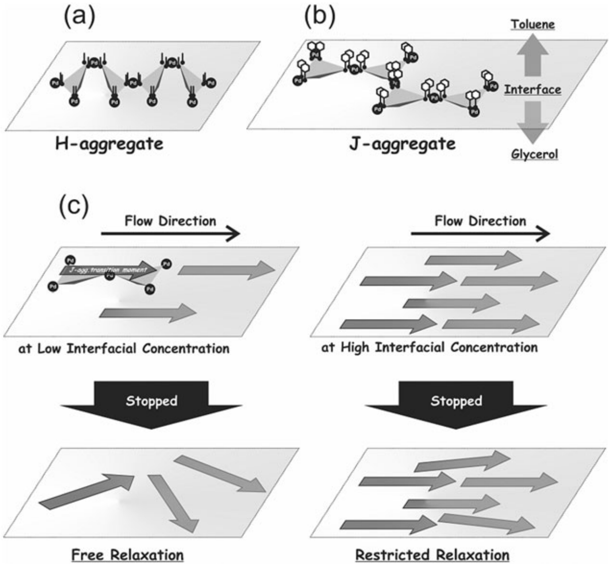
Relaxation time		Relative contributions P_i/LD (%)		
		Subpc(SBz)$_6$		
	T_i/s	1.0 × 10^{-5} M	3.0 × 10^{-5} M	1.0 × 10^{-4} M
Fast (T_1)	6.6–7.5	27.0	13.1	2.2
Slow (T_2)	292–322	42.8	45.6	29.5
Offset	> 2000	30.2	41.3	68.3

with

$$F = \ln(L/d) - 1.57 + 7\{(\ln(L/d))^{-1} - 0.28\}^2. \qquad (4)$$

Here, T is the absolute temperature, η is the solvent viscosity and Θ is the rotational diffusion constant, which is calculated from $\Theta = 1/(6T_i)$. This equation is usually valid in a bulk solution (three-dimensional), but the apparent rotational diffusion constant at the interface (two-dimensional) can be evaluated using eqn. (3) and eqn. (4).[26] The aggregate diameter d was taken to be 9 Å from the CPK model of the **Subpc(SBz)$_6$** molecule. The solvent viscosity η was taken as 500 mPa s (glycerol : water = 95 : 5 at 25 °C). The observed relaxation times T_i = 7 and 300 s correspond to aggregate lengths 1.2 and 4.7 μm, respectively. The shorter length obtained from the fast relaxation process is comparable with the length of aggregates frequently observed in electron micrographs, though it was formed at the toluene/water interface.[27] On the other hand, slower relaxation processes may be related to the increasing degree of entanglement when **Subpc(SBz)$_6$**–Pd(II) aggregate becomes less oriented.

From the experimental results and previous related studies,[11,28] we propose the shear-flow induced dichroism of the aggregates of **Subpc(SR)$_6$**–Pd(II) complexes at the toluene/glycerol interface, as described in Scheme 2; the UV-vis absorption spectra indicated that **Subpc(SEt)$_6$** and **Subpc(SBz)$_6$** molecules, reacting with Pd(II) at the interface, formed H-aggregates and J-aggregates, respectively. We thought that the **Subpc(SBz)$_6$**–Pd(II) complexes were assembled in tape-like J-aggregates dispersed at random, then oriented unidirectionally by a shear-flow force at the toluene/glycerol interface. After stopping the rotation, a relaxation to random orientation of the aggregate of **Subpc(SBz)$_6$**–Pd(II) complexes takes place at the toluene/glycerol interface. However, at high interfacial concentrations, the aggregates maintain their unidirectionally-oriented structure because their free reorientation is hindered due to their mutual steric repulsion.



Scheme 2 Schematic representations of the possible model of the interfacial aggregate of (a) **Subpc(SEt)$_6$**–Pd(II) and (b) **Subpc(SBz)$_6$**–Pd(II) complexes in the toluene/glycerol system. The triangular pyramid and black sphere represent a **Subpc** skeleton and a Pd(II) moiety, respectively. (c) Possible interfacial relaxation processes of the oriented aggregate of **Subpc(SBz)$_6$**–Pd(II) complexes after stopping the rotation at low and high interfacial concentrations. Grey arrows denote J-aggregate transition moments.

Conclusion

A new technique to observe the linear dichroism of interfacial molecules using two-phase Couette flow (TPCF) has been established in the present study. It allowed us to measure highly-oriented, Pd(II)-induced, thio-derivatised subphthalocyanine **Subpc(SR)$_6$** (R = Et (ethyl) or Bz (benzyl)) aggregates at a liquid/liquid interface. Moreover, this study demonstrated the potential of the TPCF-LD technique for measuring the relaxation kinetics of the orientation and reorientation of interfacial aggregates formed at a toluene/glycerol interface. In particular, the study of the interfacial relaxation of the aggregates of **Subpc(SBz)$_6$**–Pd(II) complexes confirmed multi-exponential behaviors, suggesting a fast relaxation of small aggregates and a slower relaxation of larger ones. We believe that this technique of using two-phase Couette flow would be applicable to the fabrication of new oriented functional materials such as highly-ordered nanocomposites, nanowires and nanocircuits.

Acknowledgements

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