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## COMMUNICATION

Ion-based assemblies of planar anion complexes and cationic Pt<sup>II</sup> complexes†

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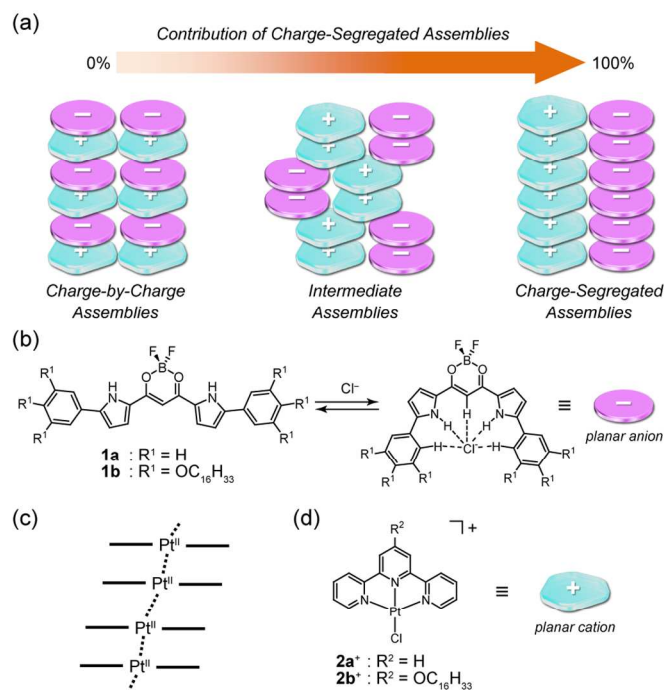
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Because the metallophilicity of attractive Pt<sup>II</sup>...Pt<sup>II</sup> interactions helps in the fabrication of columnar structures, terpyridine–Pt<sup>II</sup> complexes were used as planar counter cationic species for formation of charge-segregated assemblies using  $\pi$ -conjugated receptor–Cl<sup>−</sup> complexes as planar anions.

The arrangement of multiple components, especially  $\pi$ -conjugated species, in assembled structures is an effective strategy for fabricating functional materials, whose assembled modes and resulting properties can be controlled by choosing appropriate components.<sup>1</sup> Along with semi-conductive systems consisting of highly ordered electronically neutral molecules, an appropriate combination of charged species<sup>2</sup> can also exhibit semi-conductive behaviours. Well-designed anions and cations can provide ion-based assemblies and materials using electrostatic and other noncovalent interactions. The geometries of charged components show that planar ions are suitable building subunits of ion-based materials; they are based on various assembled modes such as charge-by-charge and charge-segregated assemblies comprising positively and negatively charged species stacked alternately and segregated, respectively (Fig. 1a, left and right).<sup>3–5</sup> In particular, charge-segregated assemblies, which cannot be easily constructed because of the electrostatic repulsion between identically charged species, would be suitable for exhibiting semi-conductive properties with high charge carrier density. Therefore, it is a synthetic challenge to even fabricate intermediate assemblies exhibiting a partial contribution from the charge-segregated mode (Fig. 1a, centre).

We have previously reported the ion-pair combination of trityl-based planar cations and planar anion complexes of pyrrole-based  $\pi$ -conjugated molecules (e.g., **1a,b**, Fig. 1b),<sup>4</sup> which provided charge-by-charge and charge-segregated assemblies as thermotropic liquid crystals, exhibiting ambipolar electric conductive properties.<sup>5</sup> However, the contribution of



**Fig. 1** (a) Conceptual diagram of charge-by-charge and charge-segregated assemblies and a candidate of their intermediate states; (b)  $\pi$ -conjugated acyclic anion receptors **1a,b** and their anion-binding mode; (c) a schematic representation of possible dimer-based 1D columnar stacking structure of planar Pt<sup>II</sup> complexes induced by attractive Pt<sup>II</sup>...Pt<sup>II</sup> interaction; (d) planar Pt<sup>II</sup> cations **2a<sup>+</sup>** and **2b<sup>+</sup>**.

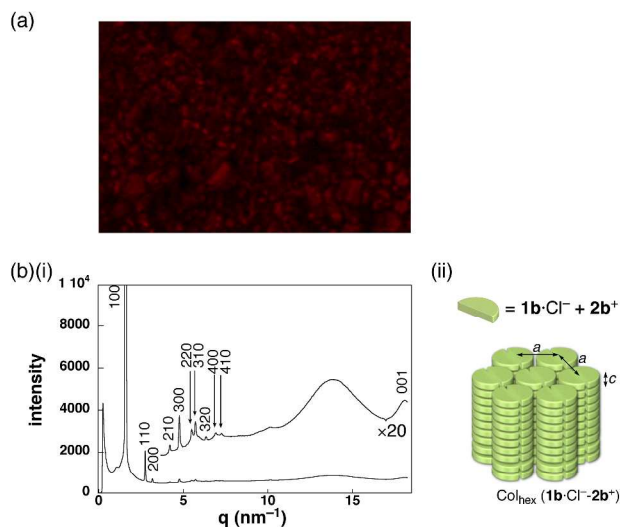
the charge-segregated assemblies was mainly derived from the relatively favourable stacking interactions between the planar cationic species, which can also attractively interact with the anion complexes to induce the contribution of the charge-by-charge assemblies. As a result, the assembled mode, corresponding to the arrangement of cations and anions, cannot be readily controlled. Therefore, it is crucial to adopt more

suitable planar cations, which form stacking structures supported by more favourable interactions between the cationic components. One of the promising candidates as the desired planar cation is a positively charged Pt<sup>II</sup> complex bearing appropriate  $\pi$ -conjugated ligand molecules. Square-planar Pt<sup>II</sup> complexes often form dimer-based 1D columnar stacking structures because of attractive Pt<sup>II</sup>...Pt<sup>II</sup> interactions (Fig. 1c).<sup>6-8</sup> This metallophilicity was attributable in part to the bonding interactions arising from the overlap of the 5d<sub>z<sup>2</sup></sub> and 6p<sub>z</sub> orbitals of adjacent Pt<sup>II</sup> centres.<sup>6a,8b</sup> Therefore, the combination of appropriate cationic Pt<sup>II</sup> complexes and planar anion complexes would result in the formation of assembled structures containing a contribution of charge-segregated assemblies.

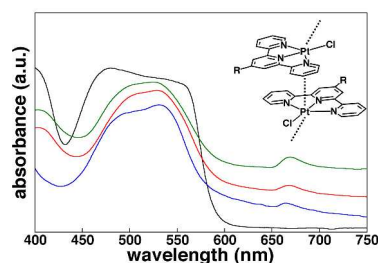
As planar cations, we focused on the Pt<sup>II</sup>Cl complexes of 2,2':6',2''-terpyridine (trpy) and 4'-hexadecyloxy-2,2':6',2''-terpyridine (trpy-C<sub>16</sub>), [Pt<sup>II</sup>(trpy)Cl]<sup>+</sup> (**2a**<sup>+</sup>) and [Pt<sup>II</sup>(trpy-C<sub>16</sub>)Cl]<sup>+</sup> (**2b**<sup>+</sup>), respectively (Fig. 1d). Treatment of **2a**·OTf with tetrabutylammonium chloride (TBACl) in CH<sub>3</sub>CN at room temperature (r.t.) afforded **2a**·Cl as a yellow-orange precipitate. On the other hand, treatment of [Pt<sup>II</sup>Cl<sub>2</sub>(PhCN)<sub>2</sub>] with 1 equiv of AgOTf followed by the addition of trpy-C<sub>16</sub> in refluxing CH<sub>3</sub>CN afforded **2b**·OTf as a red precipitate. Further treatment of **2b**·OTf with excess TBACl in CH<sub>3</sub>CN at r.t. afforded **2b**·Cl as a yellow precipitate. The ion pair **1a**·Cl<sup>-</sup>-**2a**<sup>+</sup> was obtained as an orange precipitate upon mixing **1a** and **2a**·Cl in CH<sub>3</sub>CN at r.t., whereas **1b**·Cl<sup>-</sup>-**2b**<sup>+</sup> was prepared as a red precipitate by mixing **1b** and **2b**·Cl in 1,4-dioxane at r.t. The combination of **1b** and **2a**·Cl formed a 1:1 ion pair, whereas **1a** and **2b**·Cl did not form such an ion pair. The formation of the 1:1 ion pairs of anion receptors and Pt<sup>II</sup> complexes was confirmed by <sup>1</sup>H NMR spectra and elemental analysis. Geometry optimization of **2a**<sup>+</sup> and **2b**<sup>+</sup> was carried out using DFT and PM6 calculations, respectively,<sup>10</sup> which estimated the long axis of **2b**<sup>+</sup> to be ca. 2.9 nm passing through the coordinated Cl<sup>-</sup> ion to the tip of the long alkoxy chain.

In the solid state, as revealed by single-crystal X-ray analysis, an ion pair comprising **2a**<sup>+</sup> and the Cl<sup>-</sup> complex of a diphenylboron derivative of **1a** showed the stacking dimer of **2a**<sup>+</sup>.<sup>11</sup> The Pt<sup>II</sup>...Pt<sup>II</sup> distance between adjacent **2a**<sup>+</sup> was 0.348 nm, which is similar to those of 0.332 and 0.343 nm (**2a**·Cl),<sup>8f</sup> and strongly suggests the interaction between the Pt<sup>II</sup> centres through their 5d<sub>z<sup>2</sup></sub> and 6p<sub>z</sub> orbitals. These observations indicated the possibility of the stacking structure of the cationic Pt<sup>II</sup> complexes in dimension-controlled organised structures. Furthermore, electrostatic potentials of **2a**<sup>+</sup> and **1a**·Cl<sup>-</sup> were estimated using DFT calculations.<sup>10</sup> Electrostatic potentials based on related material were found to be controlled by the stacking conditions with contributions from the charge-by-charge and charge-segregated modes.

Based on the solid-state stacking structure, the liquid crystal properties of the long-alkoxy-substituted ion pair **1b**·Cl<sup>-</sup>-**2b**<sup>+</sup> were examined using differential scanning calorimetry (DSC) and polarised optical microscopy (POM).<sup>12</sup> DSC measurement (5 °C min<sup>-1</sup>) indicated the existence of a mesophase with transition temperatures between the crystal phase and the mesophase being ca. 32 °C (1st cooling) and 28



**Fig. 2** (a) POM image of **1b**·Cl<sup>-</sup>-**2b**<sup>+</sup> at 120 °C (1st cooling); (b)(i) synchrotron XRD pattern of **1b**·Cl<sup>-</sup>-**2b**<sup>+</sup> at 120 °C (1st cooling) and (ii) a proposed model of the Col<sub>hex</sub> assemblies of **1b**·Cl<sup>-</sup>-**2b**<sup>+</sup>.



**Fig. 3** Solid-state UV/vis absorption spectra of **1a**·Cl<sup>-</sup>-**2a**<sup>+</sup> (blue: r.t.), **1b**·Cl<sup>-</sup>-**2b**<sup>+</sup> (red: r.t.; green: 100 °C) and **1b**·Cl<sup>-</sup>-TBA<sup>+</sup> (black: r.t.) and a proposed stacking structure of the Pt<sup>II</sup> complexes (inset). The structure in the inset is represented as one of its possible orientations.

°C (2nd heating), whereas transitions between the mesophase and the isotropic liquid (Iso) phase were too weak to be detected. POM measurements suggested that the transition temperature between the mesophase and the Iso was ca. 195 °C. These observations indicated a relatively wide-range mesophase compared to that of anion-free **1b**<sup>4b</sup> (164/37 °C (1st cooling) and 37/171 °C (2nd heating)). In addition, the POM image of **1b**·Cl<sup>-</sup>-**2b**<sup>+</sup> in the mesophase at 120 °C cooling from the Iso phase exhibited a mosaic-like texture (Fig. 2a).

Next, the assembled structures in the solid state and mesophase of **1b**·Cl<sup>-</sup>-**2b**<sup>+</sup> were examined using synchrotron X-ray diffraction (XRD) analysis (BL40B2 at SPring-8) at variable temperatures, whereas the ion pair **1b**·Cl<sup>-</sup>-**2a**<sup>+</sup> as a mesophase showed a complicated XRD pattern. The XRD pattern of **1b**·Cl<sup>-</sup>-**2b**<sup>+</sup> in the mesophase at 120 °C cooling from the Iso phase (Fig. 2b(i)) showed fairly sharp diffractions with *d*-spacings of the Col<sub>hex</sub> mesophase with *a* = 4.57 nm and *c* = 0.35 nm using a dimeric assembly as a building unit (*Z* = 2 for  $\rho$  = 1.36, Fig. 2b(ii)).<sup>13</sup> The in-plane spacing of **1b**·Cl<sup>-</sup>-**2b**<sup>+</sup>, which was consistent with the calculated scale of the ion-pair components, was longer than that of the Col<sub>hex</sub> mesophase of anion-free **1b** (*a* = 3.98 nm) at 170 °C (*Z* = 2.0 for  $\rho$  = 1),<sup>4b</sup>

evidently suggesting that this expansion results from the ion pairing of  $\mathbf{1b}\cdot\text{Cl}^-$  and  $\mathbf{2b}^+$ . In particular, in contrast to the (001) value of ca. 0.73 nm in the charge-by-charge assemblies of  $\mathbf{1b}\cdot\text{Cl}^-$  and the trityl-based planar cations,<sup>5a</sup> the diffraction at 0.35 nm in  $\mathbf{1b}\cdot\text{Cl}^-$ - $\mathbf{2b}^+$  strongly suggests the existence of the stacking structure consisting of identically charged species in the  $\text{Col}_{\text{hex}}$  mesophase. The first observation of the contribution from the charge-segregated assembly based on  $\mathbf{1b}\cdot\text{Cl}^-$ , in the absence of  $\beta$ -substituents, indicated a strong interaction between the cationic  $\text{Pt}^{\text{II}}$  complexes. Furthermore, the XRD pattern of  $\mathbf{1b}\cdot\text{Cl}^-$ - $\mathbf{2b}^+$  at 20 °C, which was lower than the glass-transition temperature, indicated that the  $\text{Col}_{\text{hex}}$  mesophase was frozen without a phase transition. This means that relative location of planar cation  $\mathbf{2b}^+$  remained almost unchanged at 20 °C.

Aggregated  $\text{Pt}^{\text{II}}$  complexes both in the solution and solid states exhibit characteristic absorption bands in the low-energy region because of the  $d\sigma^*(\text{Pt}_2) \rightarrow \pi^*(\text{trpy})$  metal-metal-to-ligand charge transfer (MMLCT) resulting from the  $\text{Pt}^{\text{II}}\cdots\text{Pt}^{\text{II}}$  interaction.<sup>6,7a,c</sup> Similar to the solid-state UV/vis absorption spectrum of  $\mathbf{1a}\cdot\text{Cl}^-$ - $\mathbf{2a}^+$ , recrystallized from  $\text{CH}_3\text{CN}$ , exhibiting a broad absorption band at  $\lambda_{\text{max}} = 663$  nm at r.t., the ion pair  $\mathbf{1b}\cdot\text{Cl}^-$ - $\mathbf{2b}^+$  also showed absorption maxima at 666 and 667 nm at r.t. and 100 °C, respectively, which was attributed to the MMLCT (Fig. 3). This observation strongly suggests the formation of dimeric and/or higher stacking structures of  $\mathbf{2b}^+$  in  $\mathbf{1b}\cdot\text{Cl}^-$ - $\mathbf{2b}^+$ . The observation of  $\text{Pt}^{\text{II}}\cdots\text{Pt}^{\text{II}}$  interaction was consistent with the existence of the (001) reflection with a  $d$ -spacing of 0.35 nm, because the  $\text{Pt}^{\text{II}}\cdots\text{Pt}^{\text{II}}$  distances in the aggregated structures of  $\text{Pt}^{\text{II}}$  complexes are usually in the range ca. 0.32–0.36 nm.<sup>8a,b</sup>

To investigate the importance of the stacking structure consisting of identical charged species in the mesophase of  $\mathbf{1b}\cdot\text{Cl}^-$ - $\mathbf{2b}^+$ , charge carrier mobilities were examined by field-induced time-resolved microwave conductivity (FI-TRMC) measurements.<sup>14</sup> This method features the separate evaluation of intrinsic hole and electron mobilities, where mobile charge carriers are probed by microwave under an applied pulse gate bias to metal-insulator-semiconductor devices. When holes are injected into a thin film of  $\mathbf{1b}\cdot\text{Cl}^-$ - $\mathbf{2b}^+$ , a microwave response depending on the gate bias voltages was observed (Fig. S13, ESI<sup>†</sup>). Microwave responses to electron injection were also observed, indicating the ambipolar carrier transporting nature of  $\mathbf{1b}\cdot\text{Cl}^-$ - $\mathbf{2b}^+$ . After quantifying the charge accumulation with changing the gate bias (Fig. S14–15, ESI<sup>†</sup>), we obtained the hole and electron mobility of the  $\mathbf{1b}\cdot\text{Cl}^-$ - $\mathbf{2b}^+$  thin film as  $\mu_{\text{h}} = 0.7$  and  $\mu_{\text{e}} = 0.6$   $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ , respectively, as the slope of the transient conductivity versus the number of injected charge carriers (Fig. S16, ESI<sup>†</sup>). Although the thin film of  $\mathbf{1b}^4$  also showed ambipolar characteristics, however, its hole mobility value ( $\mu_{\text{h}} = 0.4$   $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ ) was slightly smaller than that of  $\mathbf{1b}\cdot\text{Cl}^-$ - $\mathbf{2b}^+$ . Because simple binary discotic mixtures give rise to a lower structural order<sup>15</sup> and thus in principle afford poor electrical mobility, it is noteworthy that our  $\mathbf{1b}\cdot\text{Cl}^-$ - $\mathbf{2b}^+$  system possessing  $\text{Pt}\cdots\text{Pt}$  interactions provides an advantageous feature in view of its electrical conductive property.

In summary, the combination of planar anionic receptor- $\text{Cl}^-$  complexes and planar cationic  $\text{Pt}^{\text{II}}$  complexes exhibits a contribution of charge-segregated assemblies. Synchrotron XRD analysis and solid-state UV/vis absorption spectrum of  $\mathbf{1b}\cdot\text{Cl}^-$ - $\mathbf{2b}^+$  have demonstrated the existence of dimeric and/or higher stacking structures of  $\text{Pt}^{\text{II}}$  complexes in the  $\text{Col}_{\text{hex}}$  mesophase. Microwave-based conductivity measurement disclosed that  $\mathbf{1b}\cdot\text{Cl}^-$ - $\mathbf{2b}^+$  showed ambipolar characteristics and improved mobility values than  $\mathbf{1b}$  alone. Note that  $\text{Pt}^{\text{II}}$  complexes can be modified by the introduction of substituents on the trpy moiety and coordinating ligands of the  $\text{Pt}^{\text{II}}$  centre in place of the coordinating  $\text{Cl}^-$ . These approaches control the chemical and physical properties of the resulting ionic materials. Furthermore, introduction of two or more  $\text{Pt}^{\text{II}}$  centres on  $\text{Pt}^{\text{II}}$  complexes strengthens the intermolecular interaction between the  $\text{Pt}^{\text{II}}$  complexes via the multiple  $\text{Pt}^{\text{II}}\cdots\text{Pt}^{\text{II}}$  interactions. The combination of cationic  $\text{Pt}^{\text{II}}$  complexes and appropriate anionic species significantly increases the contribution of the charge-segregated assemblies in the resulting assembled structures. Further investigations into more functional materials based on ion-pairing systems are currently underway.

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## Notes and references

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† Electronic Supplementary Information (ESI) available: Synthetic procedures, DSC profiles, POM images, XRD patterns and a cif file. See DOI: 10.1039/c000000x/

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