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Novel 10,13-disubstituted dipyrido[3,2-*a*:2′,3′-*c*]phenazines and their platinum(II) complexes: highly luminescent ICT-type fluorophores based on D–A–D structures

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ABSTRACT

Novel donor–acceptor–donor (D–A–D) π-conjugated molecules based on a dipyrido[3,2-*a*:2′,3′-*c*] phenazine (dppz) skeleton were synthesized, and their luminescent properties were investigated. Introduction of various aryl substituents to the 10- and 13-positions of dppz allowed us to tune the emission properties through modulation of the intramolecular charge transfer (ICT) character on the D–A–D chromophores. Coordination of platinum(II) to the diimine site of dppz also gave rise to facilitation of the ICT to induce a significant red shift of the emission.

Luminescent molecules with organic and organometallic frameworks have so far been developed, aimed at applications in various fields such as biochemical and medicinal analyses,[1,2] chemosensory systems,[3–5] molecular logic gates,[6] organic light-emitting diodes,[7,8] and so on. As traditional fluorescent dyes, coumarines,[9] rohdamines,[10] cyanines,[11] and pyrene derivatives[12] are representative examples, and these dyes are still useful for practical applications. More recently, various types of linearly π-conjugated compounds, including π-conjugated polymers such as poly(phenylene)s,[13] poly(phenylene-vinylene)s,[14] and poly(phenylene-ethynylene)s,[15] have been eagerly developed especially as emitting materials for organic electronics, where critical tuning of HOMO and LUMO levels is necessary to achieve optimized device performance, along with color tuning for their purposes. Intramolecular charge transfer (ICT)-type compounds, consisting of donor (D) and acceptor (A) units, have often been reported, which allows us to tune emission colors by adjusting the ICT character.[16–19] Lots of electron-donating π-building blocks have been used to tune the ICT; fluorenes,[16] carbazoles,[17] and so on. On the other hand, few numbers of electron-withdrawing counterparts that serve as general acceptor building blocks have been established except for naphthalene diimide, 2,1,3-benzothiadiazole, and *N*-containing heterocycles such as pyrazine and quinoxaline.[16,20–23]

In the present Letter, we report the synthesis and photoluminescent properties of novel fluorescent compounds based on a dipyrido[3,2-*a*:2′3′-*c*]phenazine (dppz) skeleton appended with electron-donating side-arms at its 10- and 13-positions, as shown in Figure 1. As dppz is an electron-deficient polycyclic compound, it should exhibit a strong electron-withdrawing character. In addition, the diimine site of dppz allows for coordination to various transition metal ions to yield stable metal–organic complexes with special electronic properties based on d-π perturbation. Indeed,

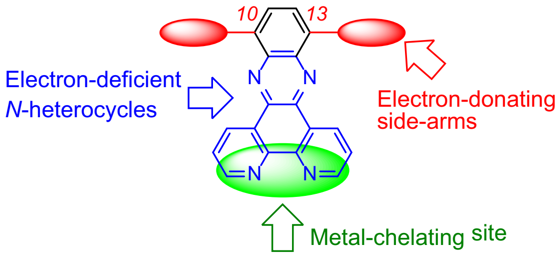

Figure 1. Molecular design of dppz-based ICT fluorophores.

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dppz derivatives have often been used as metallo-chelating ligands for DNA intercalators.[24,25] However, very few examples of dppz-based luminescent materials have been reported.[26] So we here demonstrate the development of novel highly emissive dppz-based fluorophores. We also report how the coordination of platinum(II) to the dppz fluorophore affected the emission properties through electronic perturbation in the ICT chromophoric system.

The synthesis of dppz derivatives **1a**–**g** and platinum(II) complexes **Pt-1e**–**g** is shown in Scheme 1. First, 4,7-dibromo-2,1,3-benzothiadiazole was converted to 4,7-disubstituted derivatives **2a**–**g** in excellent yields more than 80% except for **2c** (39%) by the Suzuki–Miyaura or the Sonogashira coupling reaction, followed by reduction with $LiAlH_4$ to obtain the diamines **3a**–**g** in 59–88% yields. The target compounds **1a**–**g** were prepared in 2–53% yields by condensation of **3a**–**g** with 1,10-phenanthroline-5,6-dione. The platinum(II) complexes **Pt-1e**–**g** were prepared by the reaction of **1e**–**g** with K_2PtCl_4 in 19–72% yields. The X-ray crystallographic analysis of the model compound of **Pt-1e** (i.e., **Pt-1e′**), that possesses 9,9-dimethylfluorenyl side-arms, revealed that platinum(II) coordinated to the diimine site of the dppz skeleton (Fig. 2).

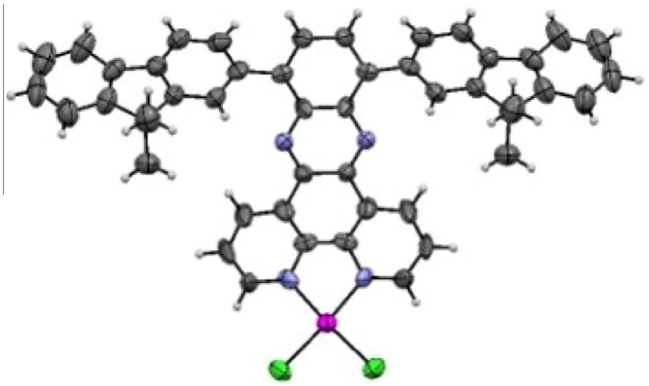


Figure 2. ORTEP view of the molecular structure for **Pt-1e′** (See Supplementary data, Table S1 and Fig. S1).

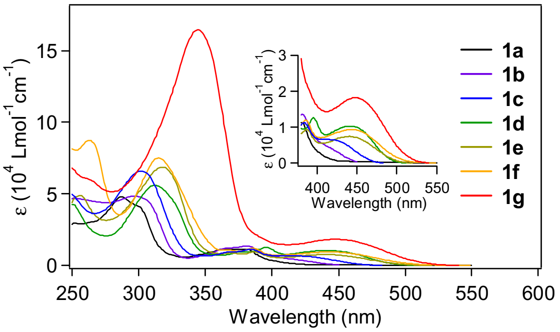
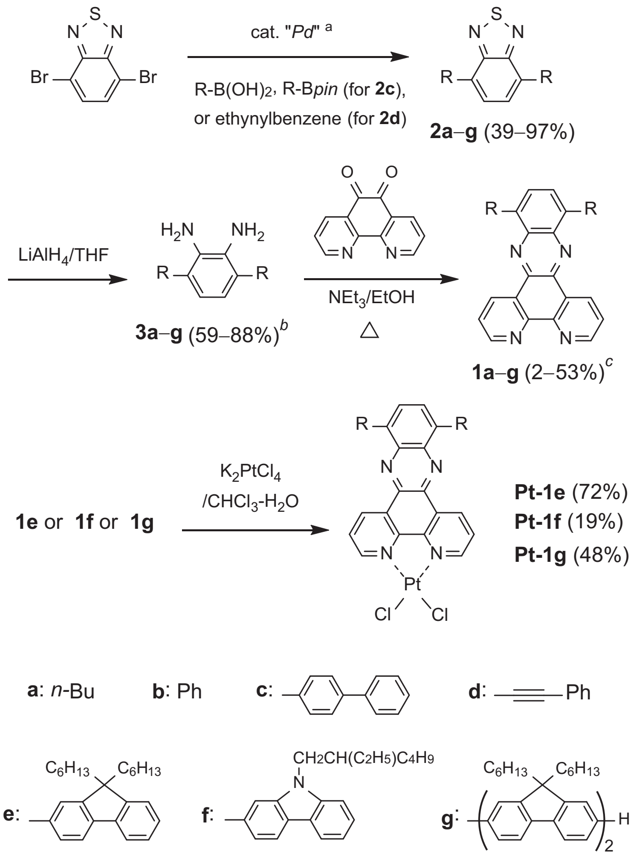


Figure 3. UV–vis absorption spectra (10 μM) of **1a**–**g** in dichloromethane at rt. Inset: enlarged view at 380–550 nm.



Scheme 1. Synthesis of **1a**–**g** and **Pt-1e**–**g**. [a]The detailed conditions are shown in Supplementary data. [b]As **3c** was poorly soluble, it was used in the next step without purification. So, the yield of **3c** was not obtained. [c]The yield of **1c** (2%) was determined as the one from **2c**.

In Figure 3 are shown electronic absorption spectra of **1a**–**g** in dichloromethane at rt, and the spectral data are listed in Table 1. The dialkylated dppz **1a** exhibited absorption bands at 250–330 nm (molar absorption coefficient ε_{abs}; 47900 M^{-1} cm^{-1} at 287 nm) and 330–450 nm (ε_{abs} = 12600 M^{-1} cm^{-1} at 363 and 381 nm), assignable to π–π* and weak ICT transitions at the dppz chromophore, respectively. On the other hand, when the butyl groups were replaced by the phenyls (i.e., **1b**), the absorption shoulder emerged at 400–450 nm. Furthermore, when extensively π-conjugated aromatic components such as biphenylyl, phenylethynyl, fluorenyl, carbazolyl, and bifluorenyl groups were introduced at the 10- and 13-positions of dppz, broad absorption bands with relatively small ε_{abs} (6500–18200 M^{-1} cm^{-1}) were additionally observed for **1c**–**g** in the longer wavelength regions (400–530 nm), that are assignable to the transition bands based on the ICT from the electron donating side-arms to the dppz core. The assignment of the absorption bands to the ICT transitions was supported by TD-DFT calculations. In Figure 4 are shown the HOMO and LUMO profiles of **1e** and **1f**. The HOMO–LUMO transition of **1a** mainly occurs on dppz (See Supplementary data, Fig. S2), whereas, in the case of **1b**–**g**, the HOMO is delocalized on the π-conjugation system including both side-arms, and the LUMO is localized on the dppz moiety. These results clearly show that the attachment of electron-donating side-arms to dppz yielded D–A–D-type ICT chromophores, and thus the onset of the absorption spectrum was comparable to the electron-donating ability of the side-arms: a couple of side-arms as stronger donors gave a more bathochromically shifted onset, that is a narrower optical band gap E_g. The electrochemical properties, obtained by cyclic voltammetry (See Supplementary data, Fig. S3 and Table S2), clearly indicated that the reduction of E_g in accordance with the increase in the electron-donating ability was caused by both destabilization of HOMO and stabilization of LUMO.

Photoluminescence (PL) spectra of **1a**–**g** in dichloromethane at rt are shown in Figure 5, and the PL quantum yields (Φ_{PL}) and emission lifetimes (τ_{PL}) are also summarized in Table 1. Weak blue and bluish green emissions ($\Phi_{PL} \leqslant 0.10$) were observed for **1a** and **1b**, respectively, indicating that the dppz without strong donor side-arms is not so emissive. On the other hand, **1c**–**g** exhibited enhanced PL (Φ_{PL} = 0.49–0.91), the emission maxima λ_{PL} of which

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