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High performance hybrid white and multi-colour electroluminescence from a new host material for heteroleptic naphthyridinolate platinum complex dopant

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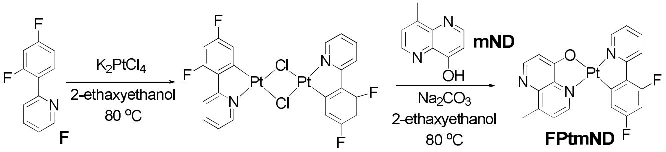
By employing a new heteroleptic platinum complex FPtmND as the single dopant in conventional CBP or new 4P-NPD host, high efficiency greenish-yellow or orange-red phosphorescent OLEDs, and high colour rendering index hybrid white OLEDs have been achieved with relatively simple device configuration.

During the past two decades, intensive studies of white organic light-emitting diodes (WOLEDs) have been developed due to their practical applications in flat panel displays[1] and electroluminescence (EL) for solid-state lighting.[2] A number of approaches have been reported to create white OLEDs.[3] Three different colour phosphorescent dopant emitters are necessary in order to achieve white EL with high efficiency (> 60~80 lm W^{-1}) and high quality (colour rendering index, CRI, > 80). However, a complicate OLED architecture is often required for such phosphorescent white EL. In addition, blue phosphorescent emitters still suffer from the lack of stability. Recently, the hybrid of blue fluorescence and yellow[4] or orange[5] phosphorescence has attracted much attention in generating white EL with long stability and simplified device structure. However, most of such hybrid WOLEDs have been based on iridium complex phosphorescent dopant. To further simplify the device structure, a single dopant (platinum complex) was used in the high efficiency all phosphorescence WOLEDs, although its CRI is ≤ 80.[6] Platinum complexes are more suitable than iridium complexes for all phosphorescence single-dopant white or high quality hybrid white OLEDs. There have been just few reports on platinum complexes in high quality (CRI > 90) hybrid WOLEDs.[7] Planar molecule geometry of platinum complex facilitates molecular aggregate and excimer formation that exhibits red-shifted emission different from the complex itself. Such emission feature of platinum complex easily broadens the EL spectra and high quality virtual sunlight often can be achieved.

Recently, Leo et al. have reported a blue fluorescent material,[8] *N*,*N*′-di-1-naphthalenyl-*N*,*N*′-diphenyl-[1,1′:4′,1″:4″,1□-quaterphenyl]-4,4□-diamine (4P-NPD), with a very high photoluminescence (PL) quantum yield (~92%) at λ_{max}^{PL} 427 nm (and a shoulder at 450 nm) and a triplet energy gap (E_T) of ~2.3 eV, which is not suitable as the host material for phosphorescence green dopant Ir(ppy)$_3$ (E_T~2.4 eV). However, orange Ir(MDQ)$_2$(acac) (E_T~2.0 eV) or yellow Ir(dhfpy)$_2$(acac) (E_T~2.2 eV) phosphorescent dopant fits quite well in the 4P-NPD host in generating hybrid WOLEDs, although unsatisfactory CRI was obtained. Up to date, 4P-NPD has never been tested for platinum complex-based OLED or WOLED until present study.

We report the synthesis, and characterization, as well as photophysical and electrochemical properties of a new heteroleptic platinum–complex **FPtmND** bearing previously known 8-methyl-1,5-napthyridine (**mND**)[9] and 2-(2,4-difluorophenyl)pyridine (**F**) as the mixed ligand (Scheme 1). With conventional 4,4'-*N*,*N*′-dicarbazolebiphenyl (CBP) or the new 4P-NPD as the host material, application of **FPtmND** for OLEDs showing multi-colour or hybrid white EL has been extensively explored.



Scheme 1 Synthesis of **FPtmND**.

Unlike the conventional CBP host material (E_T~2.55 eV), **FPtmND** dopant exhibits rather different EL behaviour in 4P-NPD. Moreover, in terms of EL efficiency, 4P-NPD as hole transporting layer (HTL) is better than conventional 1,4-bis(1-naphthylphenylamino)biphenyl (NPB) probably due to its superior hole mobility.[8c] Using **FPtmND** doped, single emitting layer (EML) OLEDs, we have demonstrated that efficient greenish yellow EL can be achieved. We have also demonstrated that high quality hybrid WOLEDs also can be achieved with **FPtmND** doped OLEDs using

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4P-NPD as both HTL and host material. Otherwise, with an appropriate combination of materials or different dopant concentration, multi-colour or white EL (see Fig. 1) can be acquired from **FPtmND** dopant and host systems (Device A~H shown in ESI).

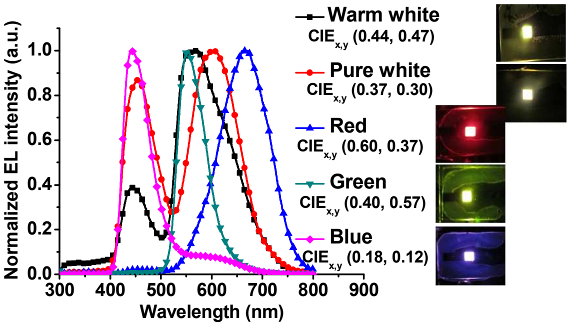

Figure 1 EL spectra and the corresponding device photos (inset on the right) of Device H (warm white), Device D with 5 wt% dopant (pure white), Device B at 50 wt% dopant (red), E (green), and Device B with 2 wt% dopant (blue).

Like most hetroleptic platinum complexes, the new platinum complex **FPtmND** was readily synthesized in a two-step procedure (Scheme 1). The detail of synthesis procedure and structural characterization can be found in ESI. The thermal stability of **FPtmND** was checked by thermogravimetric analysis (TGA). Under nitrogen atmosphere, **FPtmND** exhibited high decomposition temperature (T_d) at 332 °C, sufficiently high for OLED fabrication by vacuum-thermal-deposition process.

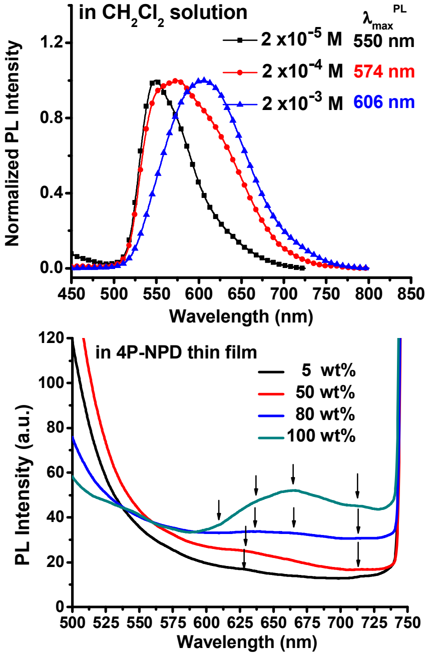

Figure 2 Top**:** Normalized solution PL spectra of **FPtmND** with varied concentration. Bottom: PL spectra of the thin film of FPtmND (100 wt%) and its 4P-NPD hosted thin film.

The emission behaviours of **FPtmND** were examined both in solution and in solid state. In a dilute solution of CH_2Cl_2 (2×10^{-5} M), **FPtmND** displayed greenish-yellow PL with λ_{max}^{PL} at 550 nm, which is reasonably ascribed to the emission of **FPtmND** in non-aggregate form (isolated molecule). When the concentration of the solution gets increased, PL becomes red-shifted (up to λ_{max}^{PL} 606 nm) and broadening (Fig. 2 top), indicative of a variety of excimer/aggregate of **FPtmND** taking place in solution. In solid state of 4P-NPD hosted thin film, **FPtmND** exhibited even more red-shifted PL with a series of recognizable signals (λ_{max}^{PL} 600 ~ 725 nm) (Fig. 2 bottom), depending on the concentration of **FPtmND** or the host material (see Fig. S9 for the PL spectra of CBP or polystyrene hosted thin films). The PL quantum yield (Φ_{PL}) of **FPtmND** was measured to be 0.13 in degassed dilute solution of CH_2Cl_2 by the optical dilute method with $[Ru(bpy)_3](PF_6)_2]$ (Φ_{PL} = 0.062) as the reference. The emission lifetime (τ) of 6.15 μs was recorded for **FPtmND** in degassed CH_2Cl_2.

The electrochemical properties of the platinum complex were investigated by cyclic voltammetry (CV) to obtain the oxidation potential (and hence HOMO energy level) of the platinum complex (see Fig. S7 and Table S1). The optical band-gap energy estimated from the absorption onset wavelength is used in the calculation of LUMO energy level of the material. The HOMO and LUMO energy levels of the **FPtmND** are thus estimated to be 5.03 eV and 2.25 eV, respectively. Based on the same method, HOMO/LUMO energy level of NPB, 4P-NPD, and CBP was estimated to be 5.1/2.0, 5.1/2.0, and 5.3/1.9 eV, respectively. Considering the charge trapping process, similar energy level alignment of **FPtmND** and 4P-NPD enables EL from both dopant and host, but it is not favored for EL from both **FPtmND** and CBP, of which difference of energy level is larger. In addition, emission from CBP is much weaker than that of 4P-NPD.

Fig. 3 shows the device configurations and the molecular structures of relevant compounds used in OLEDs of this work. Having CBP as the host material, single EML Device A and C were fabricated with configurations of ITO/NPB or 4P-NPD (40 nm)/CBP: *x*% **FPtmND** (20 nm)/TPBI (40 nm)/LiF(1 nm)/Al (150 nm), where TPBI (1,3,5-tris(*N*-phenylbenzimidazole-2-yl)benzene) is electron-transporting layer (ETL); *x* is **FPtmND** dopant concentration of 2, 5, and 8 wt%. Greenish yellow EL (λ_{max}^{EL} around 548~552 nm) matches quite well with the PL spectrum of the non-aggregated **FPtmND** in solution. No long wavelength EL beyond 600 nm was observed for dopant concentration up to 8 wt% (Fig. 4 top). However, there is a weak but discernible blue emission maximum around 420-460 nm of Device A and C with 2 wt% dopant concentration, which is ascribed to the fluorescent EL of 4P-NPD or NPB. The blue emission was largely diminished when the dopant concentration increased to 5 or 8 wt%. At 5 wt% dopant concentration, The greenish yellow (CIE$_{x,y}$ (0.42, 0.56)) Device A exhibited moderate performance of maximum external quantum efficiency of 8.9%, corresponding to a current efficiency of 33.9 cd A^{-1} and power efficiency of 10.1 lm W^{-1}. Device C displayed similar greenish yellow EL (CIE$_{x,y}$ (0.40, 0.58)) and significantly outperformed Device A, showing maximum external quantum efficiency of 15.1%, current efficiency of 58.3 cd A^{-1}, and power efficiency of 26.1 lm W^{-1}. The EL efficiency of greenish yellow FPtmND can be improved further in a double EML OLED, Device E or F, ITO/NPB or 4P-NPD (40 nm)/4P-NPD: 5% FPtmND (20 nm)/CBP: 5% FPtmND (20 nm)/TPBI (40 nm)/LiF(1 nm)/Al (150 nm). EL efficiency of Device E or F reached 16.3 or 18.2%, 63.1 or 69.7 cd A^{-1}, and 39.7 or 43.8 lm/W (Fig. 3), respectively. More extensive device data can be found in ESI. These OLED performances are relatively good when compared with other greenish yellow platinum complex-based phosphorescent OLEDs.[10]

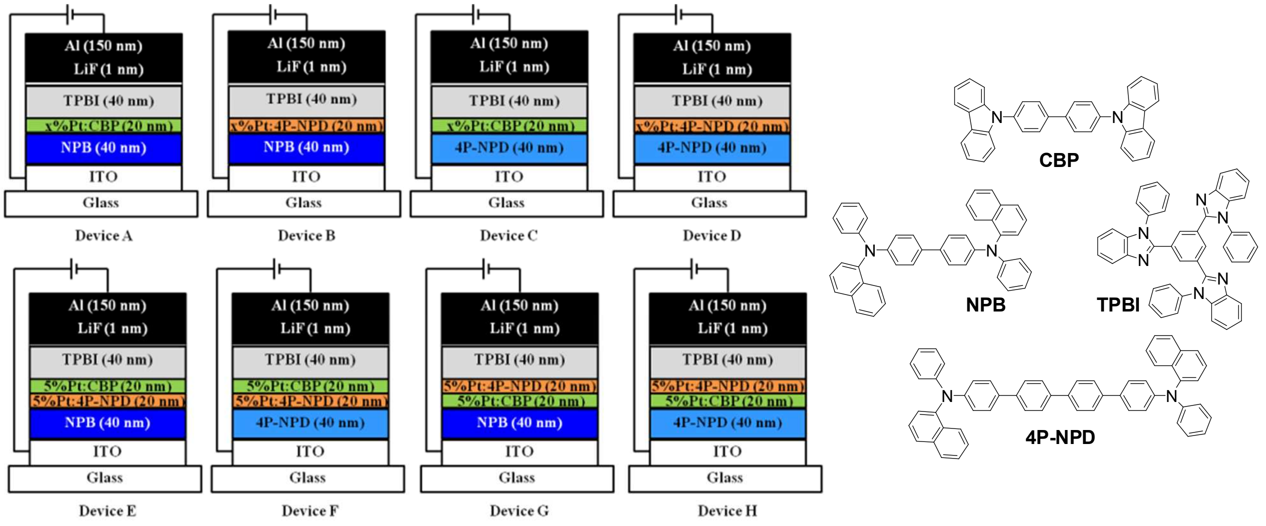

Figure 3 The device configurations (Device A-H) and the molecular structure of the relevant materials used in the devices.

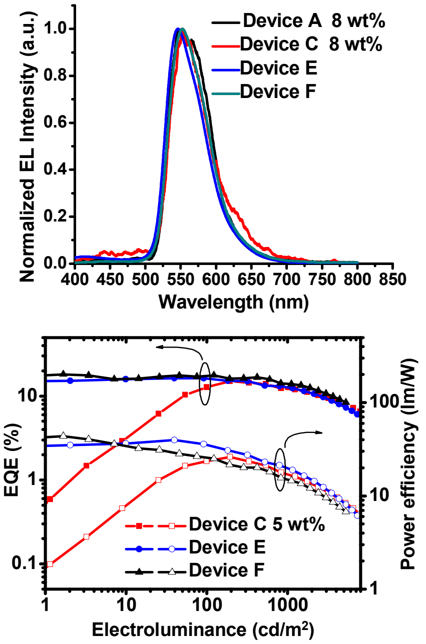

Figure 4 Top: EL spectra of Device A (8 wt%), C (8wt%), E, and F. Bottom: External quantum efficiency (EQE) and power efficiency as a function of electroluminance of Device C (5 wt%), E, and F.

Just by switching the host material CBP to 4P-NPD, Device B or D with configuration of ITO/NPB or 4P-NPD (40 nm)/4P-NPD: *x*% **FPtmND** (20 nm)/TPBI (40 nm)/LiF(1 nm)/Al (150 nm), where *x* = 2, 5, 8, or 50%, exhibited very different EL spectrum profiles (see Fig. 5). First, due to the high PL quantum yield of 4P-NPD host material, blue emission band peaked around 440~460 nm is much intense and its intensity is dopant concentration dependent. Second, with **FPtmND** dopant concentration in a range of 2~8 wt%, the EL of **FPtmND** is red-shifted to 605~616 nm and becomes especially broad, compared with the EL of Device A, C, E, and F. Inferable from the PL spectra (Fig. 2), such red-shifted and broad EL is composed of emission from non-aggregate and series of excimer/aggregate **FPtmND**. This is evident that blue emission of 4P-NPD host and greenish yellow emission of non-aggregate **FPtmND** are largely diminished when the dopant concentration is increased to 50 wt%. With such high dopant concentration, Device B actually exhibit orange-red EL with CIE$_{x,y}$ (0.60, 0.37) and a relatively mild efficiency roll-off was obtained: EQE of 9.4, 9.5, 8.6% (or power efficiency of 4.0, 3.3, 2.3 lm W^{-1}) at 100, 500, 3000 cd/m^2, respectively. Such EL performance of orange-red Device B is better than most other platinum complex-based red OLEDs reported earlier in recent years.[11]

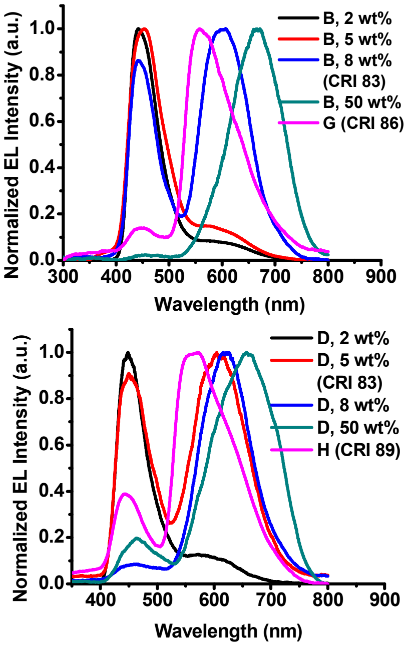

Figure 5 Normalized EL spectra of Device B and D with varied **FPtmND** dopant concentration, 2, 5, 8, and 50 wt%. EL spectra of double EML Device G and H are included.

Nevertheless, from the results of Device B and D, we have realized that having appropriate control of **FPtmND** dopant concentration, 8 wt% for Device B and 5 wt% for Device D, nearly pure white EL can be achieved, CIE$_{x,y}$ (0.39, 0.29) and CIE$_{x,y}$ (0.37, 0.30), respectively. The best EL efficiency of such white Device B and D is 5.9 and 6.1%, 11.0 and 11.3 cd/A, and 6.2 and 6.7 lm W^{-1}, respectively (Fig. 6). CRI of both devices is the same 83, which is acceptable for lighting application. Similarly, the EL performance including CRI of Device B and D can be further improved via double EML configuration, i.e., Device G or H with configuration of ITO/NPB or 4P-NPD (40 nm)/CBP: 5% **FPtmND** (20 nm)/4P-NPD: 5% **FPtmND** (20 nm)/ TPBI (40 nm)/LiF(1 nm)/Al (150 nm). With the second EML (CBP: 5 wt% **FPtmND**) of the device, the greenish yellow EL around 550~570 nm is greatly intensified with partial expense of blue fluorescent EL and orange to red excimer/aggregate phosphorescent EL. Overall, EL spectra are broadening somewhat and EL efficiency is improved further (greenish yellow emission of non-aggreagte **FPtmND** is stronger than orange-red emission of excimer/aggregate). As the results, compared with those of white Device B and D, CRI increased further to 86 and 89, maximum EL efficiency elevated to 9.3 and 11.9%, 24.1 and 29.0 cd A^{-1}, 9.6 and 12.1 lm W^{-1}, respectively (Fig. 6). However, Device G and H exhibited warm white EL, CIE$_{x,y}$ (0.44 ,0.47) and CIE$_{x,y}$ (0.41, 0.41), respectively. Device H also exhibited relatively mild efficiency roll-off: EQE of 11, 10, 9.0% (or power efficiency of 11.5, 7.9, 6.0 lm W^{-1}) at 100, 100, 3000 cd/m^2, respectively.

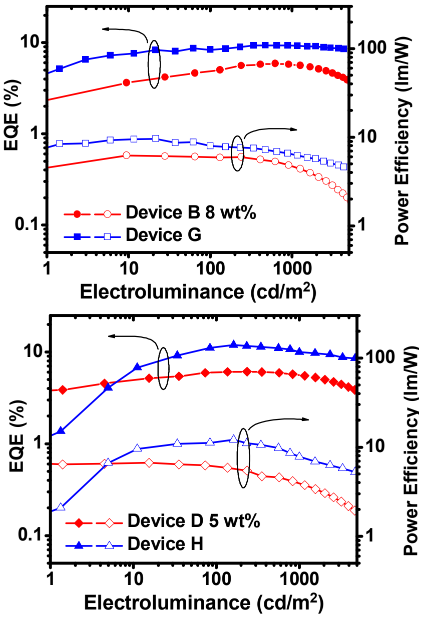

Figure 6 External quantum efficiency and power efficiency as a function of electroluminance of hybrid WOLEDs, Device B (8 wt%), Device G, Device D (5 wt%), and Device H.

In summary, a new platinum complex **FPtmND** has been synthesized and characterized. Its PL property and EL application have been scrutinized. **FPtmND** itself exhibits greenish yellow emission in dilute solution or CBP hosted thin film, in which little or moderate excimer/aggregate of **FPtmND** is formed. Particularly for EL, more pronounced excimer/aggregate of **FPtmND** was observed in 4P-NPD hosted thin film and it has red-shifted wavelength of 600~750 nm. Utilizing such emission properties of **FPtmND**, the colour of EL could be varied by controlling the concentration of the platinum complex and the type of host materials used for EMLs in the fabricated OLEDs. For instances, high efficiency greenish yellow and orange-red EL have been achieved with **FPtmND** OLEDs with CBP and 4P-NPD host, respectively. Moreover, simple architecture hybrid WOLEDs were fabricated by employing a single phosphorescence dopant **FPtmND** together with the highly fluorescent 4P-NPD host. High quality (CRI 83~89) white and warm white ELs have been achieved with mild efficiency roll-off in an electroluminance range of 100 and 3000 cd/m^2.

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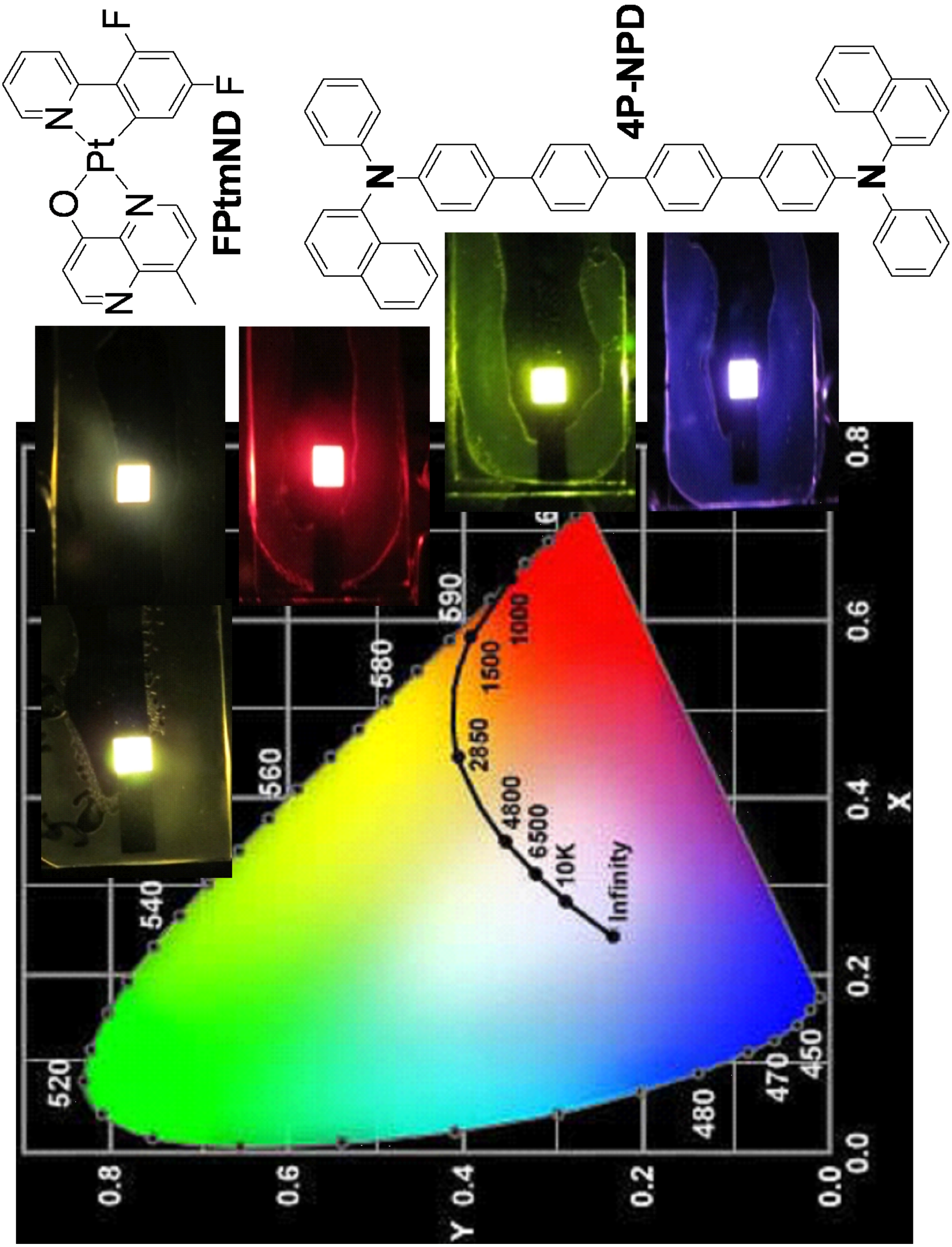
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