Electronic Supplementary Material for CrystEngComm

SUPPORTING INFORMATION

Luminescence from π–π Stacked Bipyridines through Arene-Perfluoroarene Interactions

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1. Syntheses and physical properties of 1-3.

4,4'-Diphenylethnyl-2,2'-bipyridine (1). Compound **1** was prepared using the Sonogashira cross-coupling reaction similar to previously reported procedures.[1,2] Iodobenzene (300 mg, 1.47 mmol) was added to a triethylamine solution (10 mL) of 4,4'-diethynyl-2,2'-bipyridine (100 mg, 0.49 mmol),[2] $Pd(PPh_3)_2Cl_2$ (11 mg, 15.7×10^{-3} mmol), and CuI (3 mg, 15.7×10^{-3} mmol) under a N_2 atmosphere. The reaction mixture was stirred at reflux for 6 h. The solvent was removed by distillation and the residue was extracted using dichloromethane from the aqueous phase along with a small amount of ethylenediamine. The organic layer was then dried by $MgSO_4$ and concentrated by evaporation. It was purified by flash column chromatography (silica, 99:1 CH_2Cl_2/MeOH) and crystallization from a CH_2Cl_2/hexane solution to give a white powder of **1**. Yield 76%. mp 205 °C. ^{1}H NMR (600 MHz, $CDCl_3$, TMS) δ 8.69 (d, J = 5.1 Hz, 2H, Py*H*), 8.55 (s, 2H, Py*H*), 7.58 (dd, J = 7.2 Hz, 4H, Ph*H*), 7.42 (d, J = 5.1 Hz, 2H, Py*H*), 7.42-7.39 (m, 6H, Ph*H*). EI-MS *m/z* 356 (M). IR (KBr disk, cm^{-1}) 3436, 2217, 1599, 1585, 1533, 1485, 1442, 1361, 989, 763, 754. Elemental analysis: Calcd for $C_{26}H_{16}N_2$ (%): C 87.62, H 4.52, N 7.86; found: C 87.44, H 4.60, N 8.12. It was recrystallized from benzene/hexafluorobenzene as **1**•C_6F_6, suitable for X-ray crystallography.

4,4'-Bis(pentafluorophenylethnyl)-2,2'-bipyridine (2). Compound **2** was prepared from iodopentafluorobenzene and 4,4'-diethynyl-2,2'-bipyridine using the same conditions for **1**. Yield 59%. mp 241 °C. ^{1}H NMR (600 MHz, $CDCl_3$, TMS) δ 8.74 (d, J = 4.5 Hz, 2H, Py*H*), 8.60 (s, 2H, Py*H*), 7.49 (d, J = 4.5 Hz, 2H, Py*H*). EI-MS *m/z* 536 (M). IR (KBr disk, cm^{-1}) 3421, 3068, 2926, 1586, 1517, 1498, 1359, 1123, 987, 973, 843. Elemental analysis: Calcd for

$C_{26}H_6F_{10}N_2$ (%): C 58.23, H 1.13, N 5.22; found: C 58.48, H 1.13, N 5.27. It was recrystallized from benzene/hexafluorobenzene as **2**, and suitable for X-ray crystallography.

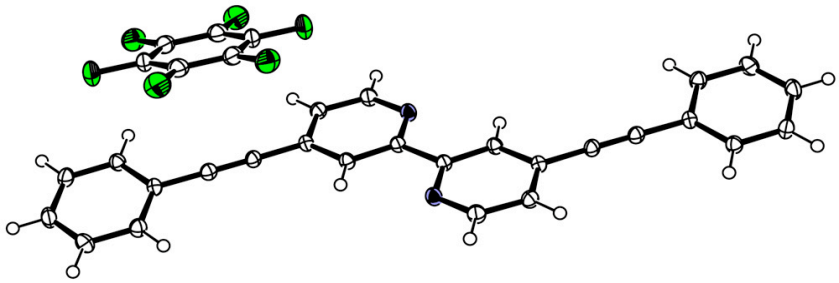
Cocrystal of 3 (= 1•2). Compounds **1** (36 mg, 0.1 mmol) and **2** (54 mg, 0.1 mmol) were completely dissolved in hot benzene (3 mL). The mixture was cooled to room temperature to give a white powder of **3**. Yield 70%. mp 220 °C. Elemental analysis: Calcd for $C_{52}H_{22}F_{10}N_4$ (%): C 69.96, H 2.48, N 6.28; found: C 70.35, H 2.53, N 6.39. It was recrystallized from benzene/hexane as 2(**3**)·C_6H_6, and suitable for X-ray crystallography.

1) T. R. Kelly, Y.-J. Lee, R. J. Mears, *J. Org. Chem.*, 1997, **62**, 2774.

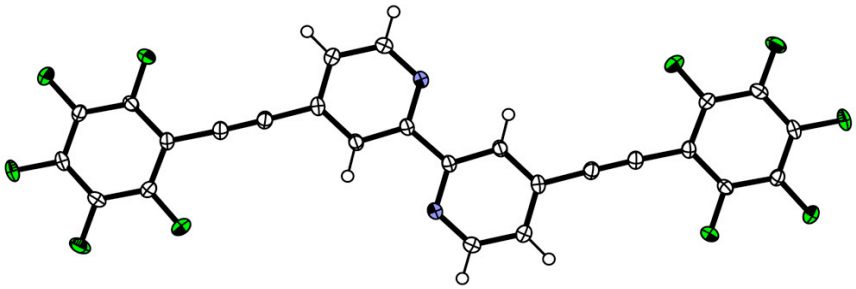
2) R. Ziessel, J. Suffert, M.-T. Youinou, *J. Org. Chem.*, 1996, **61**, 6535.

2. Crystal structures of 1 and 2.

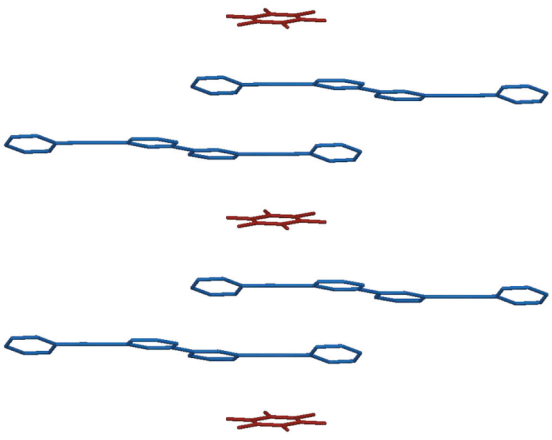
(a) ORTEP drawing of **1**·C_6F_6 with 50% probability thermal ellipsoids at 100 K.



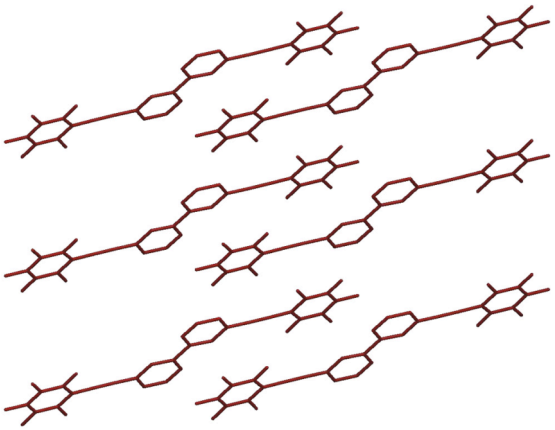
(b) ORTEP drawing of **2** with 50% probability thermal ellipsoids at 100 K.



(c) Packing structures of **1**·C_6F_6 and **2**.



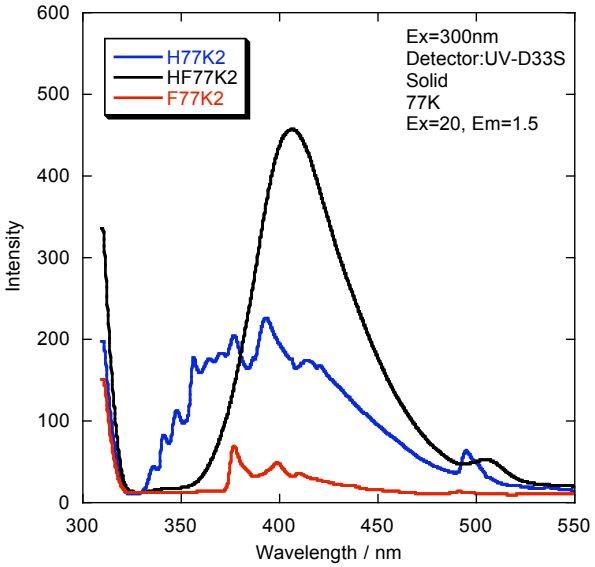
(Crystal packing of **1**·C_6F_6: view along the *b*-axis)



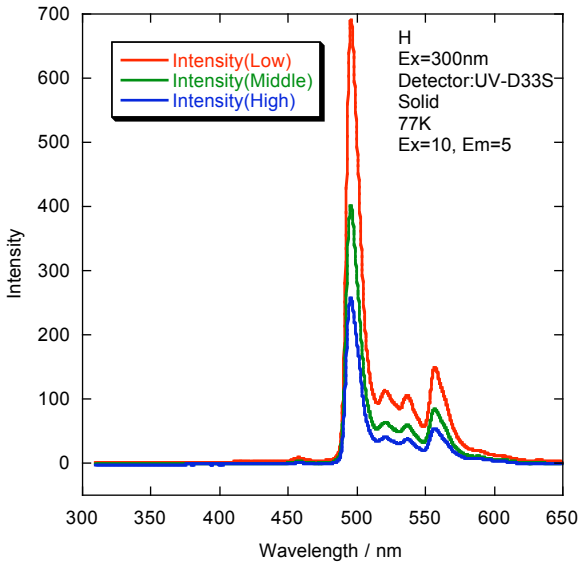
(Crystal packing of **2**: view along the *a*-axis)

3. Solid-state luminescence spectra of 1-3 at 77K.

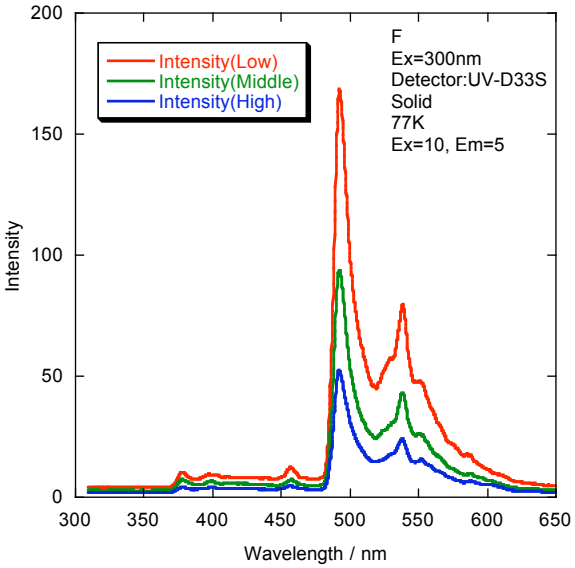
The fluorescence band around 400 nm of **1** and **2** had bibronic bands, but that of **3** was broad (Fig. a). A small peak around 500 nm appeared for each, being assigned as a phosphorescence band. The time-resolved emission spectra of **1** (Fig. b), **2** (Fig. c), and **3** (Fig. d) at 77 K were measured using a chopper. The chopper speed of the emission detector for the phosphorescence measurements was changed to 46 ms (Low), 23 ms (Middle) and 15 ms (High) intervals using a Hitachi F3010 fluorophotometer with an attachment system.



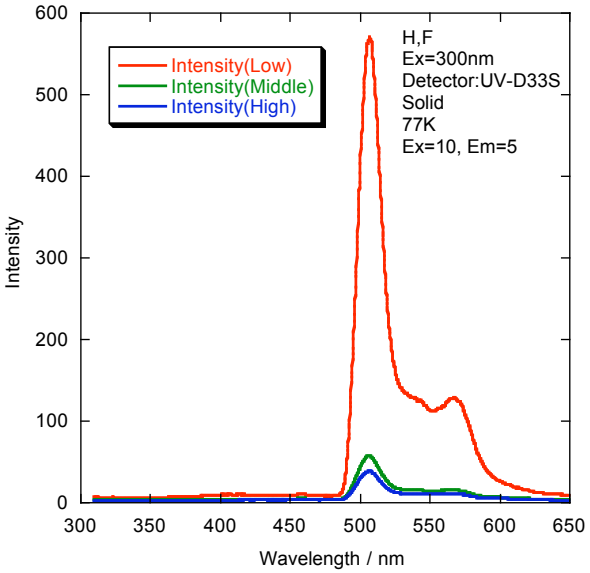
(a) Complexes **1-3** (77 K, λ_{ex}= 300 nm) without chopper.



(b) Complex **1** with chopper

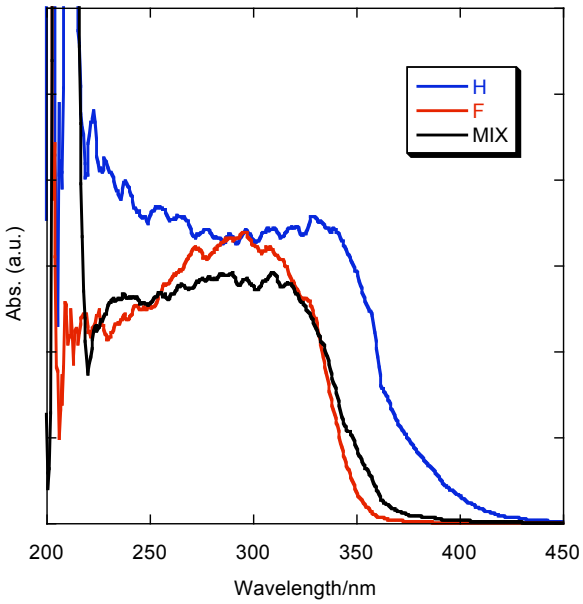


(c) Complex **2** with chopper



(d) Complex **3** with chopper

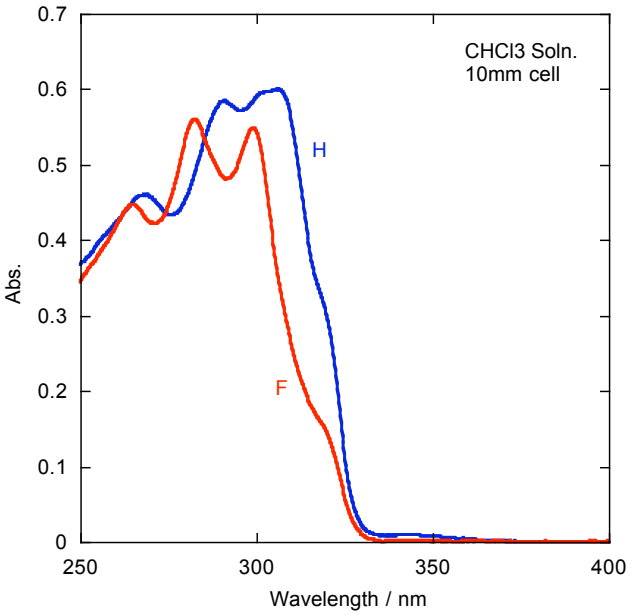
4. Absorption spectra of 1-3 (Solid: left; solution: right).



(a) Solid-state absorption spectra of **1-3**.

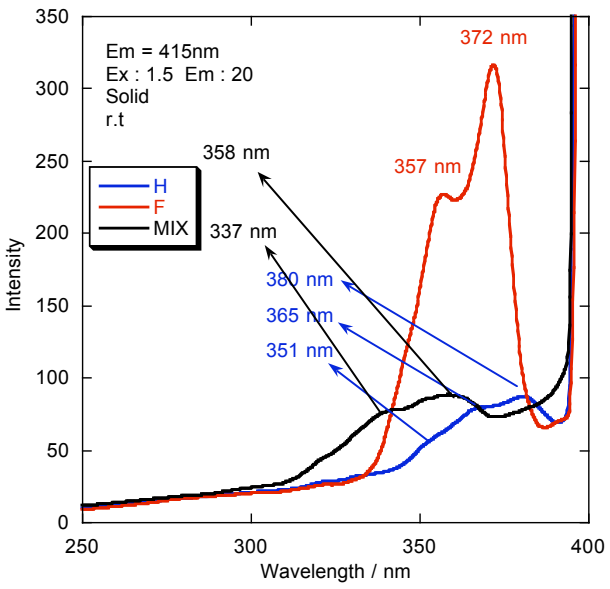
Diffused reflection spectra was exchanged by the Kbelba-Munk equation.[3]

3) P. Kubelka, F. Munk, *Z. Tech. Phys.*, 1931, **12**, 593.

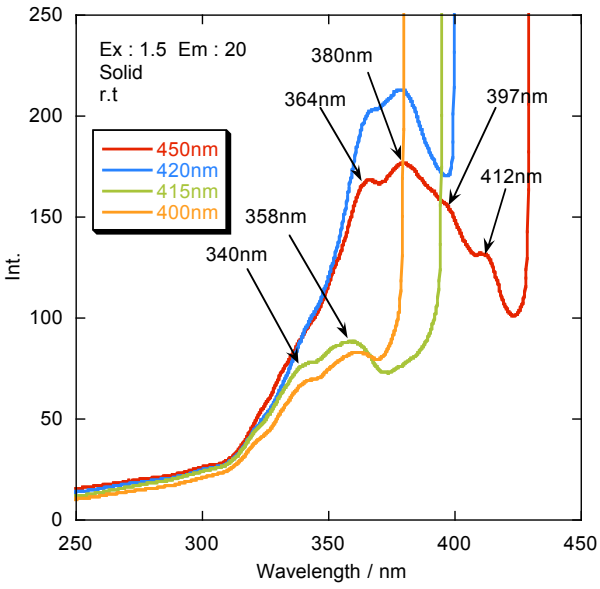


(b) Electronic absorption spectra of **1** and **2** in $CHCl_3$ at r.t.

5. Excitation spectra of 1-3.



(a) Excitation spectra of complexes **1-3** (r.t., λ_{mon}= 415 nm).



(b) Excitation spectra of Complex **3** monitored at various wavelength positions.