Supporting Information for

Multicolor Fluorescence and Electroluminescence of an ICT-type Organic Solid Tuned by Modulating the Accepting Nature of Central Core

Kai Wang, Shuo Huang, Yu Zhang, Shanshan Zhao, Hongyu Zhang* and Yue Wang State Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, Jilin University, Changchun 130012, P. R. China. Corresponding author's email: <u>hongyuzhang@jlu.edu.cn</u>

Experimental

General Information

All solvents and materials were used as received from commercial suppliers without further purification. ¹H NMR spectra were measured on Varian Mercury 300 MHz spectrometer with tetramethylsilane as the internal standard. Mass spectra were recorded on a Shimadzu AXIMA-CFR MALDITOF mass spectrometer. Elemental analyses were performed on a flash EA 1112 spectrometer. UV-vis absorption spectra were recorded by a Shimadzu UV-2550 spectrophotometer. The emission spectra of solutions were recorded by a Shimadzu RF-5301 PC spectrometer. The emission spectra of solids and films were recorded using Maya2000 Pro CCD spectrometer. The absolute fluorescence quantum yields were measured on Edinburgh FLS920 steady state fluorimeter. Differential scanning calorimetric (DSC) measurements were performed on a NETZSCH DSC204 instrument at a heating rate of 10 °C min⁻¹ from 20 to 350 °C under a nitrogen atmosphere. Thermogravimetric analyses (TGA) were performed on a TA Q500 thermogravimeter by measuring their weight loss while heating at a rate of 10 °C min⁻¹ from 25 to 800 °C under nitrogen. Electrochemical measurements were performed with a BAS 100W Bioanalytical electrochemical work station, using Pt as working electrode, platinum wire as auxiliary electrode, and a porous glass wick Ag/Ag^+ as pseudo-reference electrode with standardized against ferrocene/ferrocenium. The oxidation potential of 1 and was measured in CH₂Cl₂ solution containing 0.1 M of *n*-Bu₄NPF₆ as a supporting electrolyte at a

scan rate of 100 mV s⁻¹. The reduction potential of **1** was measured in DMF solution containing 0.1 M of n-Bu₄NPF₆ as a supporting electrolyte at a scan rate of 100 mV s⁻¹. The single crystal of **1** suitable for X-ray structural analysis was obtained by vacuum sublimation and the single crystal of **1**-TFA was obtained by slowly diffusing petroleum ether vapor into a acidified solution of 1 by excess TFA. Diffraction data were collected on a Rigaku RAXIS-PRID diffractometer using the ω -scan mode with graphite-monochromator Mo•K α radiation. The structure was solved with direct methods using the SHELXTL programs and refined with full-matrix least-squares on $F^{2,1}$ Non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were calculated and refined isotropically. The corresponding CCDC reference number (CCDC: 930942 for 1 and CCDC: 930941 for 1-TFA) and the data can be obtained free of charge from The Cambridge Crystallographic Centre Data via www.ccdc.cam.ac.uk/data_request/cif. Neutral 1.2×10^{-5} M solution was prepared in spectrophotometric grade CH₂Cl₂ and portioned equally into three quartz spectrophotometry cuvette with 4 ml neutral solution. 50 μ L HCl (12 M), TFA (13.1 M), BBr₃ (10.8 M) was added to each solution. The solution was capped, shaken, and the UV-vis and fluorescence spectra were taken immediately.

Theoretical Calculations

The ground state geometries were fully optimized by the density functional theory $(DFT)^2$ method with the Becke three-parameter hybrid exchange and the Lee-Yang-Parr correlation functional³ (B3LYP) and 6-31G* basis set using the

Gaussian 03 software package.⁴

Device Fabrication and Measurement

Before device fabrication, the ITO glass substrates were pre-cleaned carefully and treated by UV/O₃ for 2 min. Then the sample was transferred to the deposition system. The devices were prepared in vacuum at a pressure of 5 \times 10^{-6} Torr. Hole-transporting material NPB (1,4-bis(1-naphthylphenylamino)-biphenyl), hole-blocking material BCP (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) and electron-transporting material Alq₃ (tris(8-hydroxyquinolinato)aluminum) were commercially available and thermally evaporated at a rate of 1.0 Å s⁻¹. After the organic film deposition, 1 nm of LiF and 100 nm of aluminum were thermally evaporated onto the organic surface. The thicknesses of the organic materials and the cathode layers were controlled using a quartz crystal thickness monitor. All of used organic materials have been purified by vacuum sublimation approach. The electrical characteristics of the devices were measured with a Keithley 2400 source meter. The EL spectra and luminance of the devices were obtained on a PR650 spectrometer. All the devices fabrication and device characterization steps were carried out at room temperature under ambient laboratory conditions.



Fig. S1 a) The emission and b) absorption spectra of compound 1 in various solvents at ca. 10^{-5} M.



Fig. S2 a) Absorption spectra of 1 in neutral at 1.2×10^{-5} M and various acid conditions (10000 equiv of 1) in dichloromethane. b) Absorption spectra of 1 in solid before and after the contact to HCl, TFA, and BBr₃ vapor.



Fig. S3 Emission spectra of **1** at 1.2×10^{-5} M containing various acid conditions (10000 equiv of **1**) in dichloromethane (a), film (b), and solid (c) after the contact to triethylamine.



Fig. S4 ¹H NMR spectra in CDCl₃ expanded in the 7–8 ppm region of **1** (blue line) and $\mathbf{1}$ + excess TFA (green line).



Fig. S5 ¹H NMR spectra in CDCl₃ expanded in the 7–8 ppm region of 1+ excess HCl (cyan line) and 1 + excess BBr₃ (black line).



Fig. S6 DSC (a) and TGA (b) thermograms of compound 1.



Fig. S7 Cyclic voltammogram of compound 1.



Fig. S8 Emission spectra of **1** in CH₂Cl₂ at 1.2×10^{-5} M containing excess CSA (1-CSA) and film tuned by various dopant concentration of CSA.



Fig. S9 a) Current efficiencies and b) power efficiency versus current density curves for devices A1–A5.

compd	HOMO/LUMO _{cal} (eV) ^a	$\Delta E_{\rm cal} / \Delta E_{\rm opt}^{\ b} ({\rm eV})$
1	-4.81/-1.81	3.00/2.59
1 -TFA	-9.80/-7.71	2.09/1.53

Table S1 HOMO/LUMO energy levels and band gaps of the compounds

^aValues from DFT calculation. ^bOptical band gaps ΔE_{opt} were determined from the absorption onsets in the solutions.

Table S2	Crystal	data for	1	and	1-	TFA
----------	---------	----------	---	-----	----	-----

	1	1-TFA
empirical formula	$C_{40}H_{28}N_4S_2$	$C_{44} H_{38} F_6 N_4 O_8 S_2$
formula wt	628.78	928.90
<i>Т</i> , К	291(2) K	291(2) K
crystal system	monoclinic	triclinic
space group	$P2_{1}/c$	<i>P</i> -1
<i>a</i> , Å	9.6569(19)	11.445(2)
$b, \mathrm{\AA}$	10.140(2)	12.104(2)
<i>c</i> , Å	18.898(5)	17.978(4)
α,deg	90.00	77.35(3)
β ,deg	118.42(2)	76.40(3)
γ,deg	90.00	65.63(3)
<i>V</i> ,Å3	1627.5(6)	2183.8(8)
Ζ	2	2
density, Mg/m3	1.283	1.413
M (Mo K α), mm-1	0.199	0.205
θ range, deg	3.13 - 25.00	3.20 - 25.00
no. of reflcns	12103	17287
no. of unique	2848	7655
<i>R</i> (int)	0.0413	0.0422
GOF	1.051	1.089
$R1 [I > 2\sigma(I)]$	0.0401	0.1054
$wR2 [I > 2\sigma(I)]$	0.0913	0.2949
<i>R1</i> (all data)	0.0597	0.1603
wR2 (all data)	0.1000	0.3367

- SHELXTL, Version 5.1; Siemens Industrial Automation, Inc. 1997; G. M. Sheldrick, SHELXS-97, Program for Crystal Structure Solution; University of Göttingen: Göttingen, 1997.
- 2 E.Runge, E. K. U. Gross, Phys. Rev. Lett. 1984, 52, 997.
- 3 A. D. J. Becke, Chem. Phys. 1993, 98, 5648.
- 4 M. J. Frisch et al., Gaussian 03, Revision C.02, Gaussian, Inc.: Pittsburgh, PA 2003.