

Tuning the Electronic Nature of AIE (Aggregation-induced Emission) -Active Chromophore with Enhanced Electron-Transporting Property

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Experimental Section

Materials and Instrumentations

THF was distilled from sodium benzophenone ketyl under nitrogen immediately prior to use. All the chemicals and other reagents were purchased from Aldrich and used as received without further purification.

^1H and ^{13}C NMR spectra were measured on a Bruker AV 400 spectrometer in CDCl_3 or CD_2Cl_2 using tetramethylsilane (TMS; $\delta = 0$) as internal reference. UV spectra were measured on a Milton Roy Spectronic 3000 Array spectrophotometer. Photoluminescence spectra were recorded on a Perkin-Elmer LS 55 spectrofluorometer. High resolution mass spectrum (HRMS) was recorded on a GCT premier CAB048 mass spectrometer operating in MALDI-TOF mode. Thermogravimetric analysis (TGA) was carried on a TA TGA Q5500 under dry nitrogen at a heating rate of $20\text{ }^\circ\text{C}/\text{min}$. Thermal transitions were investigated by differential scanning calorimetry (DSC) using a TA DSC Q1000 under dry nitrogen at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$. Cyclic voltammogram was recorded on a Princeton Applied Research (model 273A) at room temperature. The working and reference electrodes were glassy carbon and Ag/AgNO_3 (0.1 M in acetonitrile), respectively. The solution was deactivated by bubbling nitrogen gas for a few minutes prior to electrochemical measurements. Transmission electron microscope (TEM) and electron diffraction pattern were obtained using JOEL 2010 TEM at an accelerating voltage of 200 KV. Sample was prepared by casting a drop of suspension onto copper 400-mesh carrier grid and dried in open air at room temperature.

Device fabrication and characterization

EL devices were fabricated on 80 nm-ITO coated glass with a sheet resistance of $25\Omega/\square$. Prior to load into the pretreatment chamber, the ITO coated glasses were soaked in ultrasonic detergent for 30 min, followed by spraying with de-ionized water for 10 min, soaking in ultrasonic deionized water for 30 min and ovenbake for 1 h. The cleaned samples were treated by CF_4 plasma with a power of 100 W, gas flow of 50 sccm and pressure of 0.2 Torr for 10 s in the pretreatment chamber. The samples were transferred to the organic chamber with a base pressure of 7×10^{-7} Torr without breaking vacuum for depositing a 60 nm 4,4-bis(1-naphthylphenylamino)biphenyl (NPB), a 20 nm emitter, a 10 nm 2,2',2''-(1,3,5-benzinetriyl)tris(1-phenyl-1-*H*-benzimidazole) (TPBi), and a 30 nm tris(8-hydroxyquinoline)aluminum (Alq_3), which serve as hole-transporting, light-emitting, hole-blocking, and electron-transporting layers, respectively. The samples were transferred to the metal chamber for cathode deposition which composed of 1 nm LiF capped with 100 nm Al. The light-emitting area was 4 mm^2 defined by the overlap of cathode and anode. The current density-voltage characteristics of the devices were measured by the HP4145B semiconductor parameter analyzer. The forward direction photons emitted from the devices were detected by a calibrated UDT PIN-25D silicon photodiode. The luminance and external quantum efficiencies of the devices were inferred from the photocurrent of the photodiode. The electroluminescence (EL) spectra were obtained with the PR650 spectrophotometer. All the measurements were carried out under air at room

temperature without device encapsulation.

Synthesis

2-(4-bromophenyl)-5-phenyl-1,3,4-oxadiazole was synthesized according to the reported method. (Soon Wook Cha, Seong-Ho Choi, Kyungkon Kim, Jung-Il Jin, J. Mater. Chem., 2003, 13, 1900–1904 and Changsheng Wang, Lars-Olof Pålsson, Andrei S. Batsanov, Martin R. Bryce, J. Am. Chem. Soc. 2006, 128, 3789-3799)

1-[4'-(5-phenyl-2-1,3,4-Oxadiazolyl)biphenyl-4-yl]-1,2,2-triphenylethene

(TPE-Oxa): Into a stirred mixture of 0.166 g (0.55 mmol) of 2-(4-bromophenyl)-5-phenyl-1,3,4-oxadiazole, 0.188 g (0.50 mmol) of 1-(phenyl-4-boronic acid)-1,2,2-triphenylethene, and 6 mL of 2 M Na₂CO₃ solution in 15 mL THF was added 0.01 g of Pd(PPh₃)₄ under nitrogen. The mixture was heated to 80 °C for 12 h. After cooled to room temperature, the solution was extracted with 50 mL of CH₂Cl₂ twice, washed with water, and dried over Na₂SO₄, and filtered. After filtration and solvent evaporation, the product was purified by silica-gel column chromatography using hexane/dichloromethane as eluent. A pale yellow solid was obtained in 86% yield (0.237 g). ¹H NMR (400 MHz, CDCl₃), δ (TMS, ppm): 8.19-8.14 (m, 4H), 7.72 (d, 2H, *J* = 8.4 Hz), 7.56–7.54 (m, 3H), 7.42 (d, 2H, *J* = 8.4 Hz), 7.15–7.03 (m, 17H); ¹³C NMR (100 MHz, CDCl₃), δ (CDCl₃, ppm): 164.57, 164.56, 143.95, 143.89, 143.62, 143.58, 141.56, 140.26, 137.41, 132.04, 131.99, 131.72, 131.35, 129.11, 127.78, 127.68, 127.58, 127.42, 127.34, 126.97, 126.58, 126.28, 124.00, 122.52. HRMS (MALDI-TOF): *m/z* 553.2289 [(M+1)⁺, calcd 553.2202].

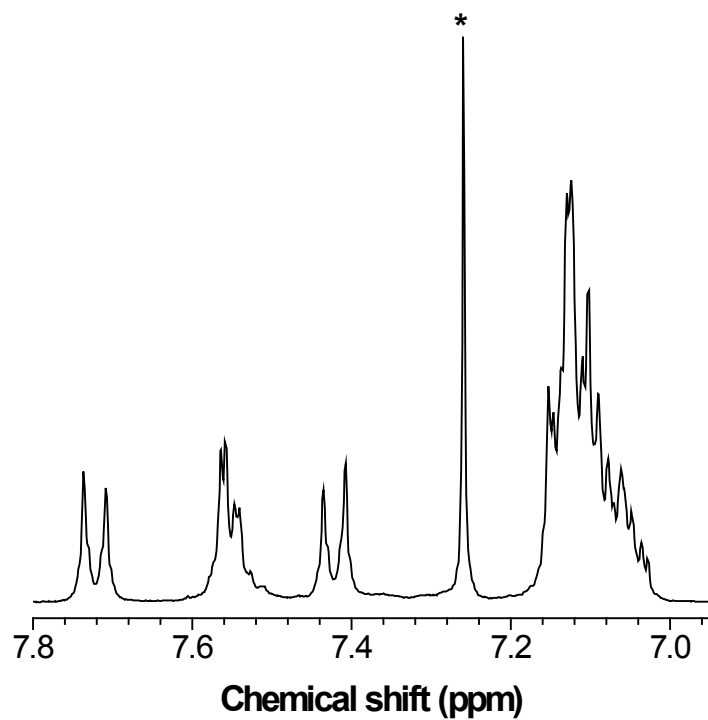


Figure S1. ^1H NMR spectrum of TPE-Ooa in chloroform- d . The solvent peak is marked with asterisk.

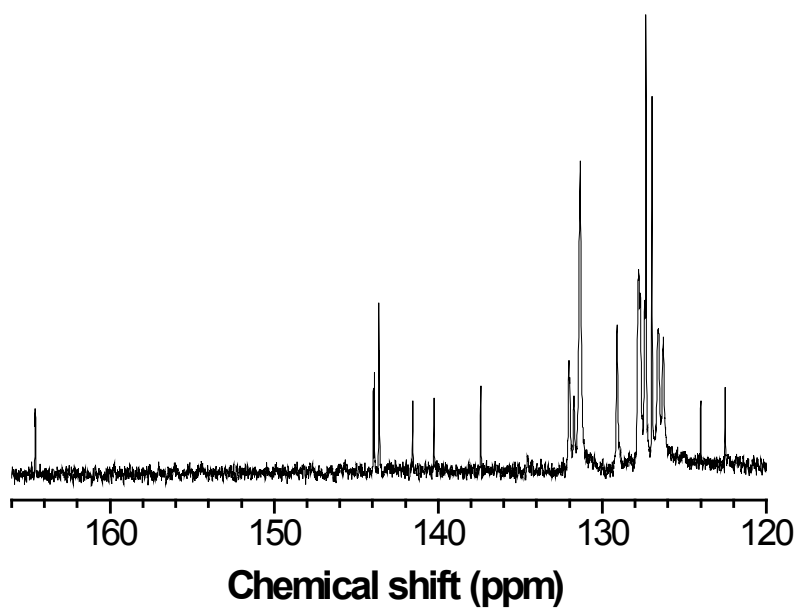


Figure S2. ^{13}C NMR spectrum of TPE-Oxa in chloroform- d .

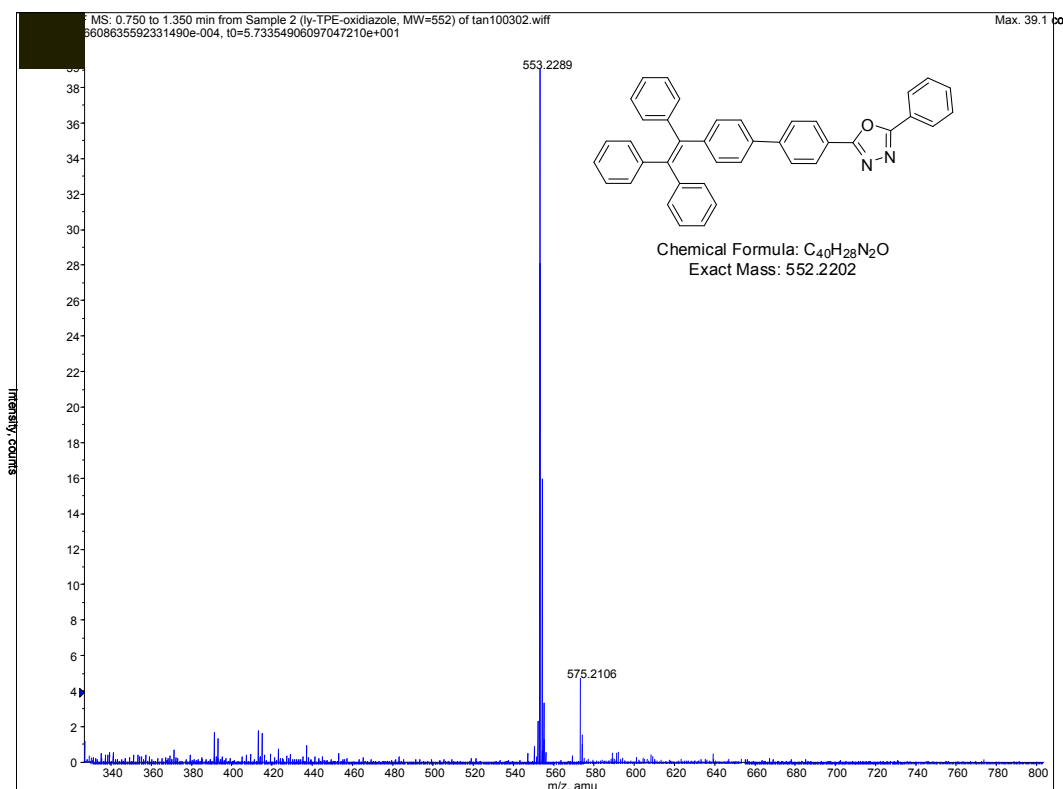


Figure S3. High resolution mass spectrum of TPE-Oxa.

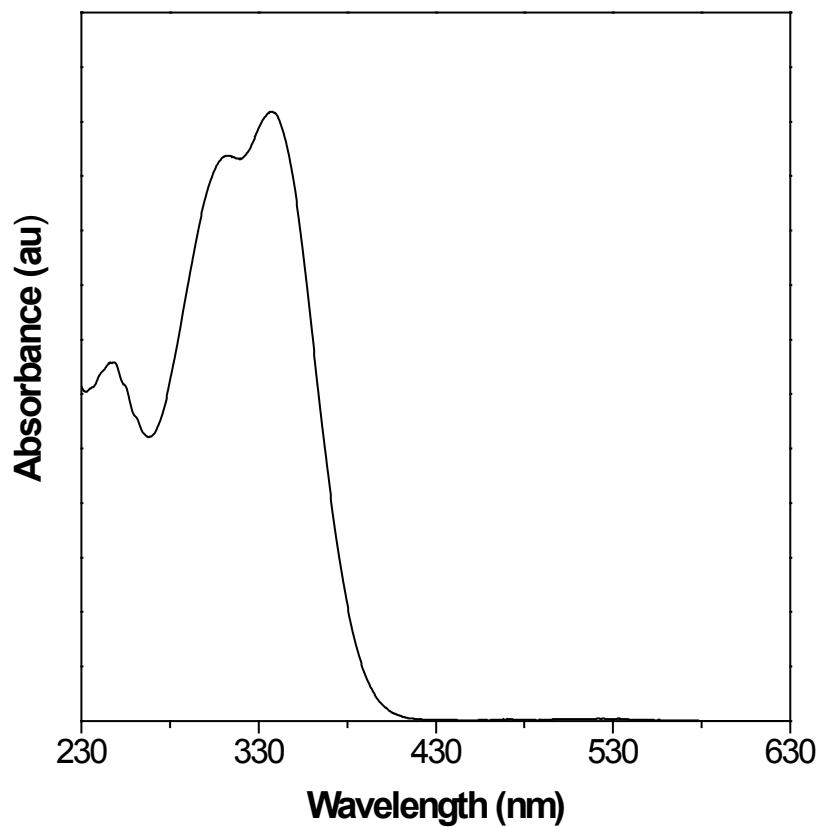


Figure S4. UV spectrum of TPE-Oxa in THF.

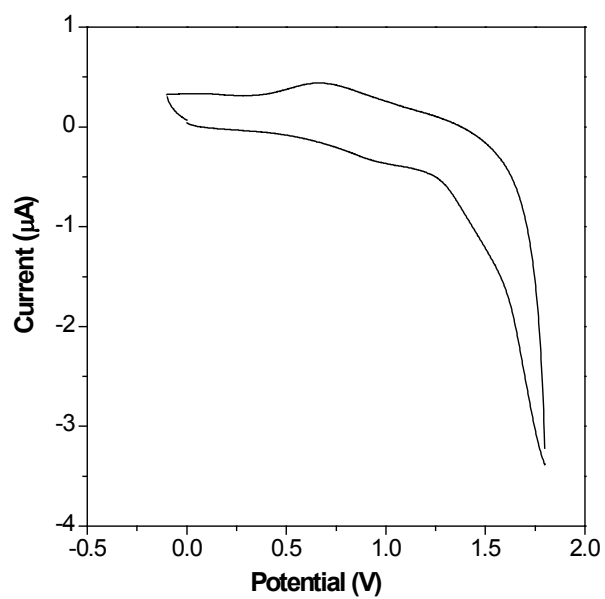


Figure S5. Cyclic voltammogram of TPE-Oxa in dichloromethane containing 0.1 M $n\text{-Bu}_4\text{NPF}_6$. Scan rate 50 mV s^{-1} .