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Supporting Information

Oxygen sensing and OLED applications of di-*tert*-butyl-dimethylacridinyl disubstituted oxygafluorene exhibiting long-lived deep-blue delayed fluorescence

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Experimental section

Instrumentals

^{1}H (300 MHz) and ^{13}C (101 MHz) NMR spectra were recorded on a Varian Unity Inova 300 apparatus at ambient temperature; spectra were analysed with the MestreNova program package. Melting points, thermogravimetric analysis, differential scanning calorimetry (DSC) measurements were carried out as described earlier [1]. Mass spectra were recorded on a Waters ZQ 2000 analytical system. Elemental analysis was performed with an Exeter Analytical CE-440 Elemental Analyzer. Density function theory (DFT) employing B3LYP/6-31G(d,p) were performed with the Gaussian 16 [2] . The molecular orbitals of the molecules were visualized using Gaussview 6. Cyclic voltammetry (CV) measurements were carried out as described earlier [3]. The absorption spectra were recorded using an Avantes AvaSpec-2048XL spectrometer. An Edinburgh Instruments FLS980 spectrometer was utilized for a measurement of the PL spectra and decay curves. The spectral measurements necessary for an estimation of PLQY values was conducted at room temperature via the FLS980 and an integrated sphere of 12 cm inside diameter. As the source of excitation, xenon lamp was used for recording emission spectra, PicoQuant LDH-D-C-375 laser was utilized for recording the PL decay curves and time-resolved PL spectra at excitation wavelength of 374 nm, microsecond lamp was used for measurements of the PL and phosphorescence spectra recorded at 77 K at excitation wavelength of 350 nm. Phosphorescence of the films of **tACR-DBO**:*m*CP was measured with delay of 0.1 ms after excitation at 77 K. Liquid nitrogen cryostat Optistat DN2 was used for photophysical investigations at the temperatures ranging from 78 to 300 K. PLQY temperature dependence was determined by integrating emission intensities and calibrating them with PLQY value measured at room temperature. By depositing on a substrate using an ultrahigh vacuum thermal evaporator (5×10^{-6} torr.), the photoelectron emission, absorption, and PL spectrum of **tACR-DBO** thin film were recorded utilizing photoelectron spectrometer (Riken Keiki Model AC-2), spectrophotometer (Hitachi U-4100), fluorescence spectrophotometer (Hitachi F-4500), respectively.

Oxygen sensing measurements

In oxygen sensing experiments, nitrogen was mixed with oxygen at different concentrations by gas-flow controller SmartTrak 50 and mass flow meter SmartTrak 100. The mixed gas flowed into a chamber with sample holder within. To ensure that a new equilibrium point had been established, several spectra (practically 3-5) were recorded under certain N_2/O_2 concentration. Equilibrium was evident when the luminescence intensity remained constant. The sensing response of the solid samples to oxygen was evaluated recording PL spectra (prompt fluorescence and TADF intensities were recorded changes by the Edinburgh Instruments FLS980 spectrometer). The dependences of emission intensity on oxygen concentration for the studied compounds were recorded under room temperature (23 °C) in the absence of water (0% of relative humidity).

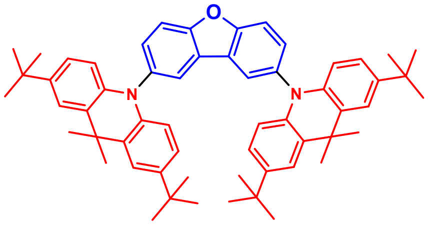
OLED fabrication and characterization

For OLED fabrication, an ultrahigh vacuum (2×10^{-6} torr.) multisource thermal evaporator was employed to deposit the high-quality organic thin films and metal electrode in sequence on an indium tin oxide (ITO) glass substrate with a sheet resistance of 30 Ω/□. The ITO glass substrate was pre-treated by using an oxygen plasma to raise the work function and reduce the hole injection barrier. After the layer deposition, the bare device was transferred into the glovebox with pure nitrogen (5N) and ultra-low oxygen content (less than 0.5 ppm). Finally, the cover glass was encapsulated with the bare device by a humidity-protection UV glue to be the finished OLED device. For measuring the device electroluminescent characterization, a luminance-current density-voltage (L-J-V) measurement system was applied comprising a multi-source meter (Keithley 2400), a spectrometer (Minolta CS-1000), and a computer with programming software. The transient electroluminescent (TREL) signal was recorded by a system comprising a photomultiplier tube (Hamamatsu H6780-20), an oscilloscope (Tektronix TDS2004C), a multi-source meter, and a computer with programming software.

Materials

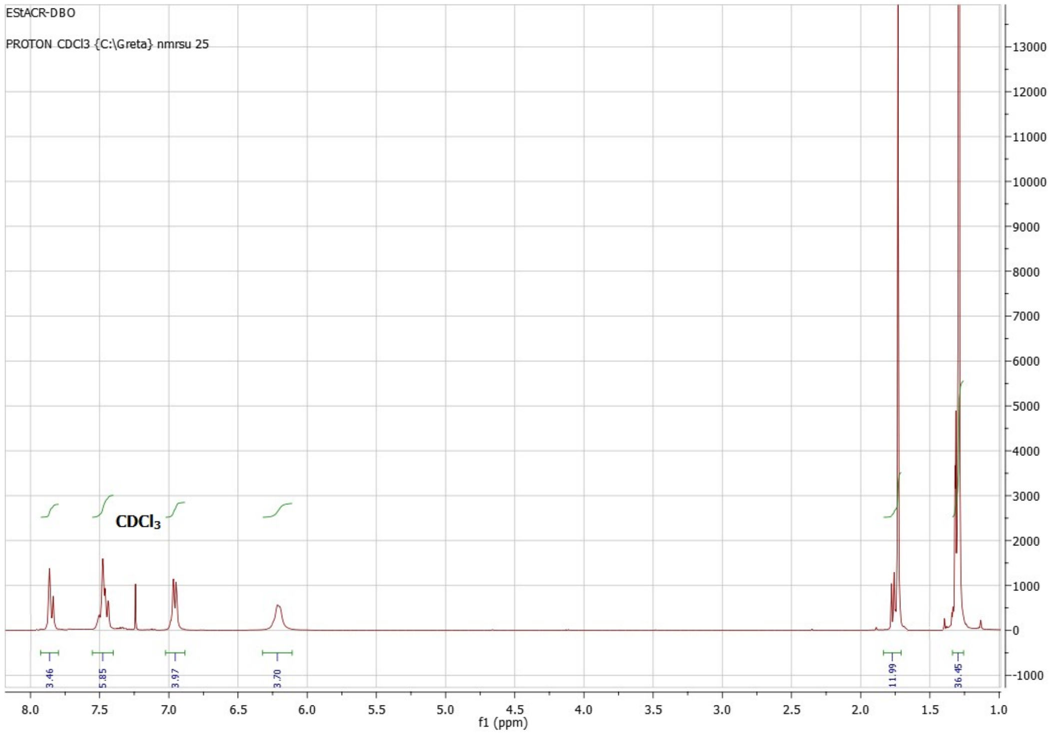
Dibenzofuran was purchased from Sigma Aldrich and used without further purification. 2,8-Dibromodibenzofuran (**1**) [4] (m.p. 187-189 °C), 2,7-di-*tert*-butyl-9,9-dimethyl-9,10-dihydroacridine (**2**) [5] (m.p. 228-229 °C) were prepared according to the published procedures.

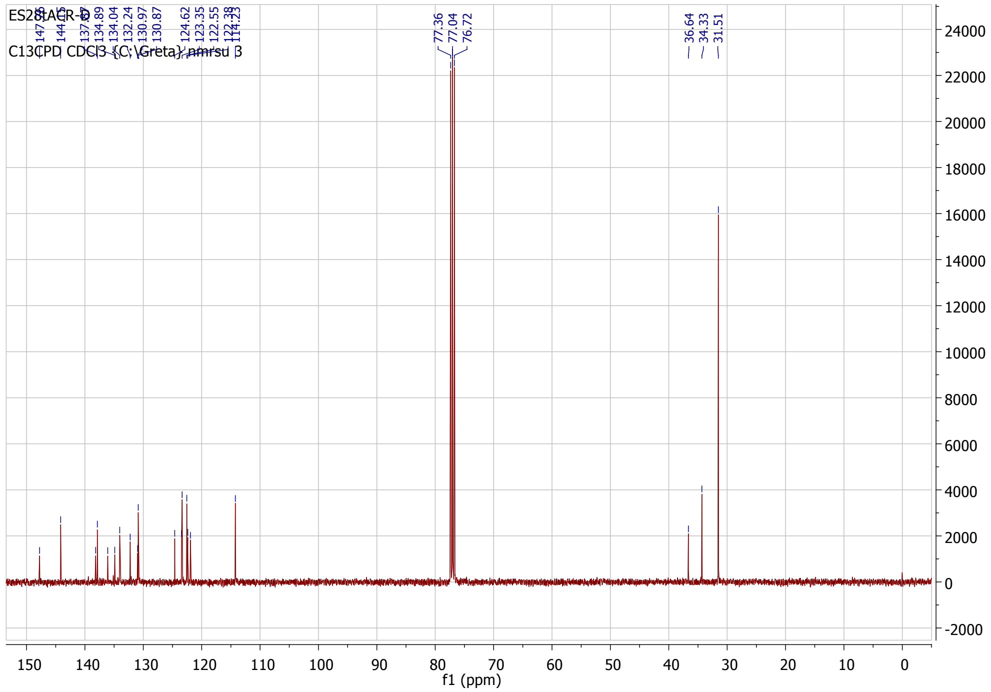
Synthesis



2,8-Bis(di(tert-butyl)-9,9-dimethyl-9,10-dihydroacridin-9-yl)-oxygafluorene **(tACR-DBO).** 2,8-Dibromodibenzofuran (**1**) (0.5 g, 1.53 mmol), 2,7-di-*tert*-butyl-9,9-dimethyl-9,10-dihydroacridine (**2**) (0.99 g, 3.06 mmol), $Pd(OAc)_2$ (0.006 g, 0.03 mmol), tri-*tert*-

butylphosphine solution (1.0 M in toluene) (0.015 g, 0.08 mmol), potasium *tert*-butoxide (0.86 g, 7.70 mmol) were dissolved in dry toluene and heated at 120 ^{o}C for 24 h. The reaction mixture was allowed to cool down to room temperature, the solvent was removed and the residue was purified by column chromatography using *n*-hexane/ethylacetate (9:1) as an eluent to obtain **tACR-DBO** as white solid (0.61 g, yield: 49%). ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ 7.85 (d, *J* = 10.5 Hz, 4H), 7.47 (t, *J* = 10.5 Hz, 6H), 6.96 (d, *J* = 6.2 Hz, 4H), 6.21 (d, *J* = 6.2 Hz, 4H), 1.73 (s, 12H), 1.29 (s, 36H). ^{13}C NMR (101 MHz, CDCl$_3$, ppm): δ 147.7, 144.1, 138.1, 137.8, 136.1, 134.8, 134.0, 132.2, 130.9, 130.8, 123.3, 122.5, 122.3, 114.2, 36.6, 34.3, 31.5. MS (APCI$^+$, 20 V), m/z: 808.3284 ([M+H]$^+$). Elemental analysis: calcd (%) for $C_{58}H_{66}N_2O$: C 86.31, H 8.24, N 3.47, O 1.98; found C 86.35, H 8.27, N 3.52.





^{1}H and ^{13}C NMR of **tACR-DBO**.

Thermal properties

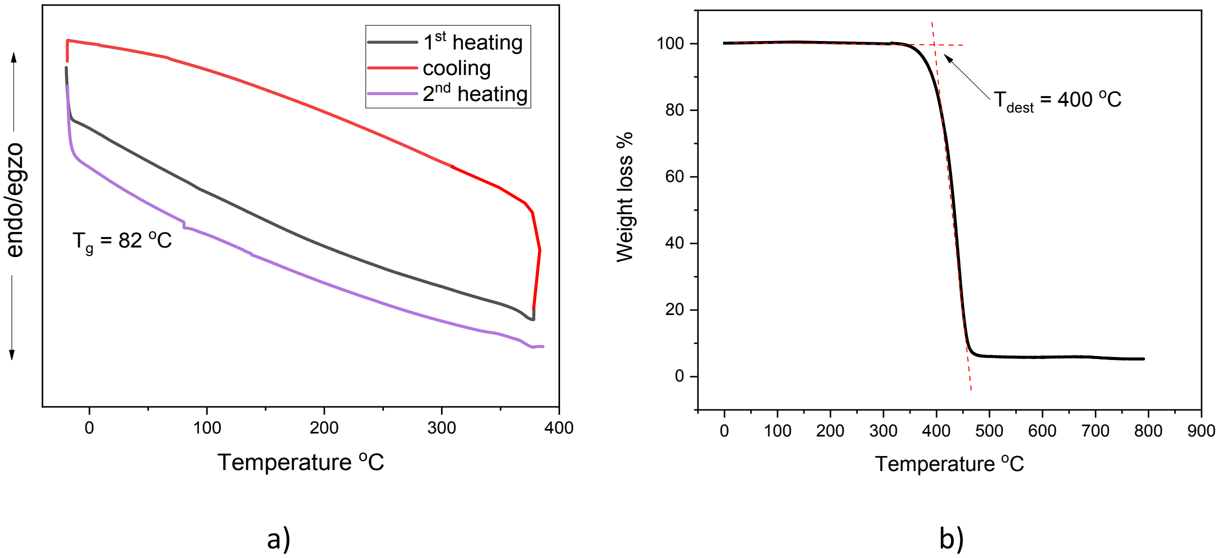
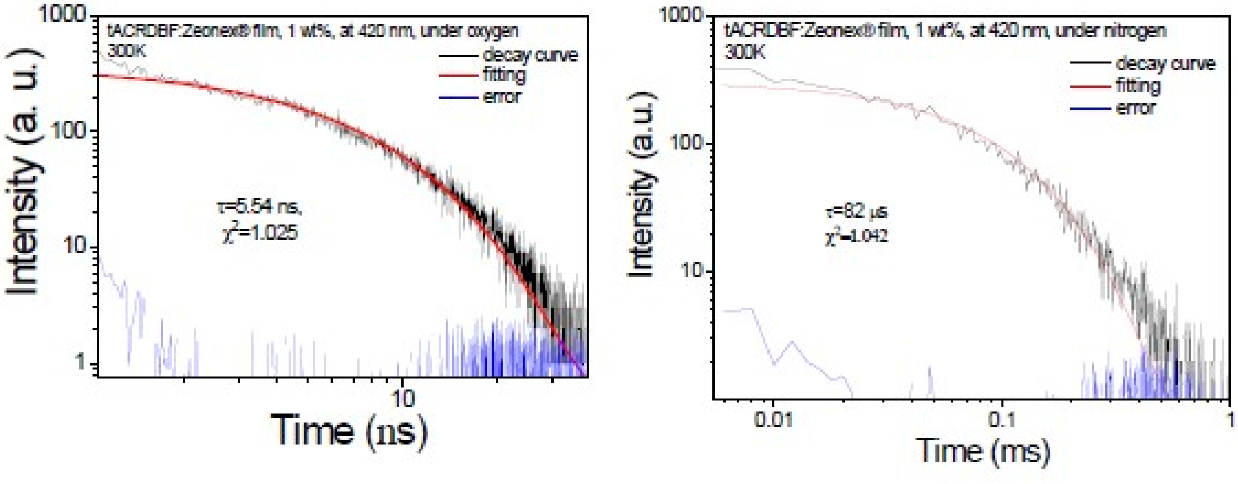


Figure S1. (a) DSC thermograms (b) and TGA curve of **tACR-DBO.**

Photophysical properties



a) b)

Figure S2. Fitting of the PL decay curves of the films of **tACR-DBO** (1 wt.%) dispersed in Zeonex®

recorded under oxygen (a) and nitrogen (b) at 300 K.

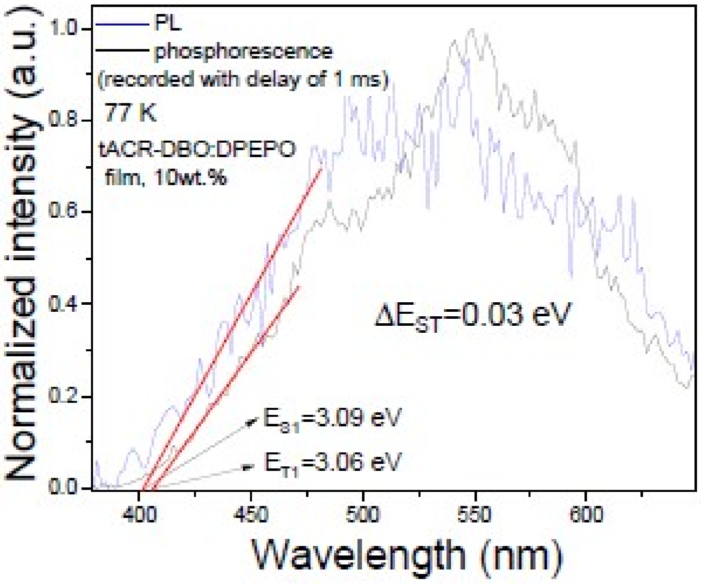


Figure S3. PL and phosphorescence spectra of the film of **tACR-DBO** (10 wt.%) dispersed in DPEPO

at 77 K.

References

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