## (Supporting Information)

# Not the Sum of their Parts: Understanding Multi-Donor Interactions in Symmetric and Asymmetric TADF Emitters

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#### Instrumentation

<sup>1</sup>H NMR (300 MHz), <sup>13</sup>C NMR (75 MHz) spectra were recorded on a Varian Unity Inova 300 apparatus. IR spectra were recorded on a Perkin-Elmer Spectrum GX II FT-IR System spectrometer. Mass spectra were recorded either on a Waters SQ Detector 2. Elemental analysis was performed with an Exeter Analytical CE-440 Elemental Analyzer. Melting points were recorded on Electrothermal MEL-TEMP melting point apparatus. Differential scanning calorimetry (DSC) measurements were carried out using a DSC Q2000 calorimeter (TA Instruments) under nitrogen environment. Thermogravimetric analysis (TGA) was performed on a TA Instruments Q50 apparatus under nitrogen gas. Cyclic voltammetry measurements were performed on a μ-Autolab Type III potentiostat (EcoChemie, Netherlands). Electrochemical experiments were carried out at room temperature using a three-electrode cell consisting of a platinum coil as counter electrode, a glassy carbon working electrode, and a silver wire as reference electrode. 0.1 M solution of tetrabutylammonium hexafluorophosphate (n-Bu<sub>4</sub>NPF<sub>6</sub>) was used as supporting electrolyte at a scan rate of 100 mVs<sup>-1</sup>. For the measurements, silver reference electrode was calibrated against ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox couple as an internal standard.<sup>1</sup>

#### **Xray methods**

The X-ray single crystal data for all compounds have been collected using  $\lambda$ MoK $\alpha$  radiation ( $\lambda$ =0.71073Å) on a Bruker D8Venture (Photon100 CMOS detector, I $\mu$ S-microsource, focusing mirrors) diffractometer equipped with a Cryostream (Oxford Cryosystems) open-flow nitrogen cryostat at the temperature 120.0(2)K. All structures were solved by direct method and refined by full-matrix least squares on F<sup>2</sup> for all data using OLEX2<sup>2</sup> and SHELXTL<sup>3</sup> software. All non-hydrogen atoms were refined in anisotropic approximation, hydrogen atoms were placed in the calculated positions and refined in riding mode. Crystal data and parameters of refinement are listed in Table SX1. Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-2088958, 2088959, and 2088960.

#### **Optical methods**

Steady-state absorption and emission spectra were measured using a double beam Shimadzu UV-3600 UV/VIS/NIR spectrophotometer and a Horiba Jobin Yvon Fluorolog-3 spectrofluorometer (with Quanta- $\Phi$  integrating sphere for PLQY measurements). Time-resolved measurements were performed using a spectrograph and a Stanford Computer Optics 4Picos ICCD camera, where samples were excited with a Nd:YAG laser (EKSPLA), 10 Hz, 355 nm.

#### **OLED** methods

Organic light-emitting diodes (OLEDs) were fabricated on patterned indium-tin-oxide (ITO) coated glass (VisionTek Systems) with a sheet resistance of  $15 \Omega/cm^2$  using vacuum thermal evaporation. The substrates were sonicated for 15 minutes each in acetone and then IPA. After oxygen-plasma cleaning, the substrates were loaded into a Kurt J. Lesker Super Spectros 200 deposition chamber. All organic and cathode layers were thermally evaporated at a pressure below  $10^{-7}$  mbar, at evaporation rates in the range of 0.1-0.5 A/s. The materials used for the device fabrication were: N,N'-bis-(naphthalene-1-yl)-N,N'-bis(phenyl)benzidine (NPB, Lumtec), 4,4-(diphenylsilanediyl)bis(N,N-diphenylaniline) (TSBPA,

Lumtec), 1,3,5-tris(N-phenylbenzimidazol-2-yl)benzene (TPBi, Lumtec), bis[2-(diphenylphosphino)phenyl]ether oxide (DPEPO, Sigma Aldrich), lithium fluoride (LiF, Sigma Aldrich), and aluminium (Al, Alfa Aesar) which were either purchased from the companies pre-sublimed or sublimation purified before use (Creaphys DSU05). The evaporated devices were encapsulated under inert atmosphere using UV-curable epoxy (DELO Katiobond) along the outer edges of the active emitting area with a glass coverslip. Characterization of OLED devices was conducted in a 10-inch integrating sphere (Labsphere) coupled with a calibrated fibre spectrometer (Ocean Optics USB4000) and connected to a Keithley 2400 source measure unit.

#### Materials synthesis and characterization

2,5-Dichlorobenzonitrile, 2,6-dichlorobenzonitrile tri-*tert*-butylphosphine ( $P(t-Bu)_3$ ) solution (1.0 M in toluene), palladium(II) acetate ( $Pd(OAc)_2$ ), sodium *tert*-butoxide (*t*-BuONa) were purchased from Fluorochem, Aldrich and used as received. 9,10-Dihydro-9,9-dimethylacridine (**a**) was synthesized as described earlier.<sup>4</sup>

The target compounds (o,m)ACA and (o,o)ACA were prepared in yields of 58-61% through a Pd-catalyzed Buchwald-Hartwig cross-coupling reaction between 9,10-dihydro-9,9-dimethylacridine and 2,5dichlorobenzonitrile or 2,6-dichlorobenzonitrile. Compounds (o,m)ACA and (o,o)ACA were purified by column chromatography and crystallization. The compounds were found to be soluble in common organic solvents such as chloroform, acetone, tetrahydrofuran.

**2,5-Bis(9,9-dimethyl-9,10-dihydroacridin-10-yl)benzonitrile** ((*o,m*)**ACA**). 2,5-Dichlorobenzonitrile (0.5 g, 2.91 mmol), 9,9-dimethyl-9,10-dihydroacridine (1.28 g, 6.10 mmol),  $Pd(OAc)_2$  (0.03 g, 0.14 mmol), tri-*tert*-butylphosphine solution (1.0 M in toluene) (0.05 g, 0.29 mmol), sodium *tert*-butoxide (0.56 g, 5.81 mmol) and 20 ml of toluene were heated at 120 °C for 24 h under nitrogen. After cooling the reaction mixture was diluted with chloroform and the organic phase was washed with water. The solvent was removed and the residue was purified by column chromatography using *n*-hexane/ethylacetate (6:1) as an eluent and crystallized from the eluent mixture of solvents to obtain (*o,m*)**ACA** as light crystals. FW = 517.68 g/mol; yield 0.91 g, 61%); m.p. 279-280 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 7.88 (t, *J* = 4.0 Hz, 1H), 7.82 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.53 – 7.42 (m, 4H), 7.09 – 6.94 (m, 8H), 6.35 (d, *J* = 8.1 Hz, 2H), 6.21 (d, *J* = 8.1 Hz, 2H), 1.69 (s, 6H), 1.64 (s, 6H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 143.4, 142.2, 140.2, 139.8, 137.9, 137.7, 136.1, 131.4, 130.8, 126.7, 125.6, 125.5, 121.8, 121.6,

118.7, 115.3, 114.3, 113.2, 36.2, 30.8. MS (APCI<sup>+</sup>, 20 V), m/z: 519 ([M+H]<sup>+</sup>). Elemental analysis calcd (%) for C<sub>37</sub>H<sub>31</sub>N<sub>3</sub>: C, 85.85; H, 6.04; N, 8.12; Found: C, 85.82; H, 6.01; N, 8.14.

**2,6-Bis(9,9-dimethyl-9,10-dihydroacridin-10-yl)benzonitrile** ((*o*,*o*)**ACA**). A procedure similar to that used for (*o*,*m*)**ACA** was used with 2,6-dichlorobenzonitrile (0.5 g, 2.91 mmol). The residue was purified by column chromatography using *n*-hexane/ethylacetate (6:1) as an eluent and crystallized from the eluent mixture of solvents to obtain (*o*,*o*)**ACA** as yellow crystals. FW = 517.68 g/mol; Yield: 0.86 g, 58%; m.p. 276-277 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 8.16 (t, *J* = 7.6 Hz, 1H), 7.75 (d, *J* = 7.6 Hz, 2H), 7.54 (d, *J* = 7.6 Hz, 4H), 7.15 – 6.96 (m, 8H), 6.33 (d, *J* = 7.6 Hz, 4H), 1.74 (s, 12H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 147.3, 139.8, 136.1, 133.5, 130.8, 126.6, 125.6, 121.7, 120.1, 113.4, 113.1, 36.1. MS (APCI<sup>+</sup>, 20 V), m/z: 519 ([M+H]<sup>+</sup>). Elemental analysis calcd (%) for C<sub>37</sub>H<sub>31</sub>N<sub>3</sub>: C, 85.85; H, 6.04; N, 8.12; Found: C, 85.81; H, 6.08; N, 8.14.



Figure S1 <sup>1</sup>H and <sup>13</sup>C NMR spectra of (*o*,*m*)ACA.



Figure S2 <sup>1</sup>H and <sup>13</sup>C NMR spectra of (*o*,*o*)ACA.

#### **Thermal properties**

(*o*,*m*)ACA and (*o*,*o*)ACA were characterized by DSC and TGA. The temperatures of transitions are showed in Table S1. DSC thermograms of (*o*,*m*)ACA and (*o*,*o*)ACA are shown below.

On the first heating scan the sample of (o,m)ACA melted at 284 °C and formed glass upon cooling. In the second heating scan the glass transition temperature (T<sub>g</sub>) of amorphous sample was observed at 95 °C, and on further heating an exothermic peak due to crystallization signal was observed at 155 °C to give the same crystals as obtained by crystallization from solution which melted at 284 °C. (o,o)ACA was isolated after the synthesis as crystalline substance. The first DSC heating scan of this compound revealed endothermal melting signal at 280 °C. In the following heating scans only the signal of melting was observed at 280 °C TGA curves of (o,m)ACA and (o,o)ACA are also shown below, and confirmed that investigated isomers are thermally stable with moderate thermal decomposition temperatures (T<sub>dest</sub>) of 355-363 °C. It indicates that (o,m)ACA and (o,o)ACA can to be used for device fabrication by vacuum thermal evaporation technology, which can improve the film morphology, and prolong the life time of the devices.



Figure S3 (a) DSC thermograms of (o,m)ACA, (left), (o,o)ACA (right) and (b) TGA curves.

Compound		T <sub>g</sub> , [°C] <sup>c</sup> (2 <sup>nd</sup> heating		T,onset [°C]e
Compound	1 <sub>m</sub> , [ C]	scan)	1 cr, [ C]	
( <i>o</i> , <i>m</i> )ACA	284, 284 <sup>b</sup>	95	155	363
( <i>o</i> , <i>o</i> )ACA	280, 280 <sup>b</sup>	-	164	338

Table S1 Thermal characteristics of (*o*,*m*)ACA and (*o*,*o*)ACA.

<sup>a</sup>  $T_m$  is melting temperature at the scan rate of 10 °C/min, N<sub>2</sub> atmosphere. <sup>b</sup> the second heating. <sup>c</sup>  $T_g$  is glass-transition temperature. <sup>d</sup>  $T_{cr}$  is thermal destruction temperature. <sup>e</sup>  $T_d^{onset}$  is the temperature of onset of thermal degradation at the scan rate of 20 °C/min, N<sub>2</sub> atmosphere.

#### **Electrochemical properties**

The electrochemical properties of compounds (o,m)ACA and (o,o)ACA were probed by cyclic voltammetry (CV) measurements. The cyclic voltammograms are shown below. All the electrochemical data are listed in Table S2. During the anodic scan (o,m)ACA and (o,o)ACA showed quasireversible oxidation waves with an oxidative onset potential of 0.70 eV compared to ferrocene, and this oxidation process could be assigned to the oxidation of the electron-donating acridinyl moiety in both compounds. During the cathodic scan, an irreversible reduction process was detected, which should be due to the reduction of the cyanobenzene moiety. The identical ionization potential (IP<sub>CV</sub> = 5.50 eV) and electron affinity (EA<sub>CV</sub> = 2.64 eV) values of isomers (o,m)ACA and (o,o)ACA were calculated. Accordingly, the electrochemical band gap ( $E_g^{el}$ ) was determined to be 2.86 eV.



Figure S4 CV curves of (*o*,*m*)ACA and (*o*,*o*)ACA.

Table S2 Electrochemical characteristics of (*o*,*m*)ACA and (*o*,*o*)ACA.

Compound	E <sup>ox</sup> <sub>onset</sub> vs Fc/V	E <sup>red</sup> <sub>onset</sub> vs Fc/V	IP <sub>CV</sub> /eV <sup>[a]</sup>	EA <sub>CV</sub> /eV <sup>[b]</sup>	$\mathrm{E}_{g}^{el}/\mathrm{eV}^{[\mathrm{c}]}$
(o,m)ACA	0.70	-2.16	5.50	2.64	2.86
(0,0)ACA	0.70	-2.16	5.50	2.64	2.86

<sup>[a,b]</sup> Ionization potential and electron affinity values estimated according to  $IP_{CV} = (E_{onset}^{ox} + 4.8)$ [eV], (where,  $E_{onset}^{ox}$  is onset oxidation potential versus the Fc/Fc<sup>+</sup>).  $EA_{CV} = (E_{onset}^{red} + 4.8)$  [eV], (where,  $E_{onset}^{red}$  is onset reduction potential versus the Fc/Fc<sup>+</sup>).  $E_{Fc/Fc}^+$  for (*o*,*m*)ACA is 0.14 V;  $E_{Fc/Fc}^+$  for (*o*,*o*)ACA is 0.33 V. <sup>[c]</sup>  $E_{g}^{el} = IP_{CV} - EA_{CV}$ .

### Single Crystal X-ray Crystallography

Crystals of (o,m)ACA and (o,o)ACA suitable for X-ray diffraction were grown by slow cooling of a saturated MeCN solution. The sample (o,o)ACA consisted of crystals of two types which turned out to be different, probably concomitant, polymorph modifications of mono-acetonitrile solvate of (o,o)ACA, (o,o)ACA1(triclinic) and (o,o)ACA2(orthorhombic) respectively. The structure (o,m)ACA contains two crystallographically independent molecules with slightly different conformations.



Figure S5 Solid-state structure of (*o*,*m*)ACA (left) and (*o*,*o*)ACA (right).

 Table S3 Crystal data and structure refinement parameters.

Compound	(0,0)ACA1	(0, <i>0</i> )ACA2	( <i>o,m</i> )ACA
Empirical formula	C <sub>39</sub> H <sub>34</sub> N <sub>4</sub>	C <sub>39</sub> H <sub>34</sub> N <sub>4</sub>	C <sub>37</sub> H <sub>31</sub> N <sub>3</sub>
Formula weight	558.70	558.70	517.65
Temperature/K	120.0	120.0	120.0
Crystal system	triclinic	orthorhombic	triclinic

Space group	P-1	Pbca	P-1
a/Å	9.9656(5)	7.7358(4)	13.5538(9)
b/Å	11.4738(6)	16.6382(8)	15.0403(10)
c/Å	14.4020(7)	47.574(2)	16.1212(11)
α/°	84.809(2)	90	68.888(2)
β/°	81.366(2)	90	79.242(3)
γ/°	69.555(2)	90	63.233(2)
Volume/Å <sup>3</sup>	1524.26(13)	6123.2(5)	2736.1(3)
Ζ	2	8	4
$\rho_{calc}g/cm^3$	1.217	1.212	1.257
μ/mm <sup>-1</sup>	0.072	0.072	0.074
F(000)	592.0	2368.0	1096.0
Reflections collected	31707	68047	49804
Independent refl., R <sub>int</sub>	8102, 0.0388	6666, 0.0995	11872, 0.0687
Data/restraints/parameters	8102/0/393	6666/0/393	11872/0/729
Goodness-of-fit on F <sup>2</sup>	1.026	1.099	1.030
Final R <sub>1</sub> , $[I \ge 2\sigma(I)]$	0.0467	0.0622	0.0626
Final wR <sub>2</sub> , [all data]	0.1234	0.1241	0.1726
Largest diff. peak/hole / e Å <sup>-3</sup>	0.30/-0.31	0.26/-0.22	0.74/-0.33

## Photophysical and optoelectronic properties



Figure S6 Time-resolved spectra and decay fitting of (o,m)ACA in 25% DPEPO film



Figure S7 Time-resolved spectra and decay fitting of (0,0)ACA in 25% DPEPO film



**Figure S8** OLED device roll-off comparison. Both traces are normalized by their individual values of  $EQE_{max}$ . Also shown are device materials (top right), as well as mCP-host device performance (black) compared to DPEPO-host (red) for (*o*, *o*)ACA.



Figure S9 Absorbance spectra in DPEPO films and various sdilute solutions (dichloromethane, toluene, cyclohexane, chloroform). The low energy edge of the main donor band is redshifted for (o,m)ACA (~300 to 325 nm) in all cases, attributed to the underlying *p*D-D state. The bottom right diagram shows representative proposed components of the overall spectra.



**Figure S10** Photoluminescence spectra in various solvents: cyclohexane (CHX), toluene (TOL), chloroform (CFM) and dichloromethane (DCM).

## References

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