## Supporting Information

# V-shaped donor-acceptor organic emitters. A new approach towards efficient TADF OLED devices.

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## **SI-1** Materials and methods

General Remarks. All reagents and solvents were purchased from commercial sources and were used as received unless otherwise noted. Reagent grade solvents (CH<sub>2</sub>Cl<sub>2</sub>, hexane, ethyl acetate) were distilled prior to use. For water-sensitive reactions solvents were dried using Solvent Purification System from MBraun (https://www.mbraun.com/us/). Transformations with moisture and oxygen sensitive compounds were performed under a stream of argon. The reaction progress was monitored by means of thin layer chromatography (TLC), which was performed on aluminium foil plates, covered with Silica gel 60 F254 (Merck) or Aluminium oxide 60 F254 (neutral, Merck). Products purification was done by means of column chromatography with Kieselgel 60 (Merck) or Aluminium oxide (Fluka). The identity and purity of prepared compounds were proved by <sup>1</sup>H NMR and <sup>13</sup>C NMR spectrometry as well as by HRMS spectrometry (via EI-MS) and IR spectroscopy. NMR spectra were measured on Bruker AM 500 MHz, Bruker AM 600 MHz, Varian 600 MHz or Varian 400 MHz instruments with TMS as internal standard. Chemical shifts for <sup>1</sup>H NMR are expressed in parts per million (ppm) relative to tetramethylsilane ( $\delta$  0.00 ppm), CDCl<sub>3</sub> ( $\delta$  7.26 ppm). Chemical shifts for <sup>13</sup>C NMR are expressed in ppm relative to  $CDCl_3$  ( $\delta$  77.16 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, td = triplet of doublets, q = quartet, p = quintet, hept=septet, m = multiplet), coupling constant (Hz), and integration. EI mass spectra were obtained on AutoSpec Premier spectrometer. IR spectra were recorded on JASCO FT/IR-6200 spectrometer.

Photophysics. UV-vis spectra were recorded on a Shimadzu UV-2550 spectrophotometer. Steady-state emission spectra were recorded on Jobin Yvon Horiba Fluoromax 3, with solvent studies performed in clean 1 cm path-length photoluminescence cuvettes (Arieka Cells) and temperature dependent film photoluminescence films studies performed on within a liquid N<sub>2</sub> cooled cryostat (Janis Research). Photoluminescence spectra were calibrated for detector efficiency using company supplied, instrument specific calibration files. The emitter materials was also degassed in toluene solvent using a custom made 1 cm path-length degassed cell stoppered with a Young tap and degassed using 5 freeze/thaw/pump cycles. The photoluminescence quantum yield (PLQY) of emitters in solvent and in solid state was determined integrating sphere. Solid-state samples were prepared as 1% w/w ratio emitters in Zeonex<sup>®</sup> polymer host on clean/dry sapphire disc substrates. Phosphorescence, prompt fluorescence (PF), and delayed fluorescence (DF) spectra and decays were recorded using nanosecond gated luminescence and lifetime measurements (from 400 ps to 1 s) using either third harmonics of a high energy pulsed DPSS laser emitting at 355 nm (Q-Spark A50-TH-RE). Emission was focused onto a spectrograph and detected on a sensitive gated iCCD camera (Stanford Computer Optics) having a sub-nanosecond resolution. PF/DF time-resolved measurements were performed by exponentially increasing gate and integration times. Temperature-dependent experiments were conducted using an helium cryostat (Janis Research) under a vacuum. Time-resolved measurements were performed by exponentially increasing the gate and delay times of iCCD Stanford Computer Optics 4Picos camera from laser excitation. The delay and integration times are set at a time longer than the previous sum of delay and integration time to avoid overlap. As the next step, the curve is corrected by integrating the measured spectra to obtain proper luminescence decay profile. Every point represents the collected emission spectra of respective emitting specie.

**Devices**. NPB (*N*,*N*'-di(1-naphthyl)-*N*,*N*'-diphenyl-(1,1'-biphenyl)-4,4'-diamine) was used as a Hole Injection Layer (HIL) and Hole Transport Layer (HTL). TPBi 2,2',2"-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) was introduced as an Electron Transport Layer (ETL). Lithium fluoride (LiF) and aluminium were used as the cathode. Organic semiconductors and aluminium were deposited at a rate of 1 Ås-1, and the LiF layer was deposited at 0.1 Ås-1. CBP 4,4'-bis(N-carbazolyl)-1,1'-biphenyl was used as hosts for all emitters. All materials were purchased from Sigma Aldrich or Lumtec and were purified by temperature-gradient sublimation in a vacuum. OLEDs have been fabricated on pre-cleaned, patterned indium-tin-oxide (ITO) coated glass substrates with a sheet resistance of 20  $\Omega$ /sq and ITO thickness of 100 nm. All small molecules and cathode layers were thermally evaporated in a Kurt J. Lesker SuperSpectros 200 evaporation system under pressure of  $10^{-7}$  mbar without breaking the vacuum. The sizes of pixels were 4 mm<sup>2</sup>, 8 mm<sup>2</sup> and 16 mm<sup>2</sup>. Each emitting layer has been formed by co-deposition of dopant and host at the specific rate to obtain 10% content of the emitter. The characteristics of the devices were recorded using a 6-inch integrating sphere (Labsphere) inside the glovebox connected to a Source Meter Unit and Ocean Optics USB4000 spectrometer.

**Electronic structure calculations.** In order to aid in the interpretation of spectroscopic data, the optical and electronic properties of compounds **4a**–**4d** were characterized with the use of electronic structure simulations. In preparation for the calculation of electronic excitation spectra, the ground-state equilibrium geometries were optimized at the density functional theory (DFT) level. Afterwards, the vertical excitation spectra were calculated with the use of the spin-opposite-scaled algebraic-diagrammatic construction method of second order (SOS-ADC(2)). [1-5] The SOS-ADC(2) method has previously been found to give accurate predictions for the energies of intra- and intermolecular charge transfer states of various organic donor-acceptor compounds and molecular clusters, [6-9] and we expect it to be reliable for the calculation of the optical properties of the WDE compounds.

The DFT calculations were performed in the computational chemistry software package Gaussian 16, Revision A.03. [10] The B3LYP exchange-correlation functional [11] was employed in combination with the def2-SVP basis set. [12] In the course of the geometry optimizations, the energies and gradients were corrected for dispersion effects via the 'D3' semiempirical correction scheme of Grimme and coworkers. [13] Due to the high computational demands of the SOS-ADC(2) method, the methyl and *tert*-butyl substituents in

all four compounds were deleted and replaced with hydrogen atoms. Furthermore, we found it necessary to impose  $C_s$  symmetry on the geometries of compounds **4a**, **4b**, and **4c**. In the case of compound **4d**, the markedly non-planar geometry of the electron-donating group makes it impossible to impose  $C_s$  symmetry, and we were unable to calculate the vertical excitation spectrum of that compound. In any case, the electronic excitation spectrum of **4d** is expected to be similar to that of **4b**. The nature of each optimized stationary point was determined by calculating the vibrational modes of the molecule.

The subsequent SOS-ADC(2) calculations were carried out with the program Turbomole, Turbomole, version 6.3.1., [14] taking advantage of the frozen core and resolution of the identity [15-18] approximations. A restricted Hartree-Fock (RHF) reference determinant was used. For reasons of computational tractability, the relatively small 6-31G(d) basis set was employed. The default auxiliary basis set [19] for the cc-pVDZ basis set [20] was used as the auxiliary basis. For each compound, we calculated the lowest four excited states per symmetry group (A' or A'') and per multiplicity manifold (singlet or triplet), for a total of sixteen excited states.

The electronic structures of the relevant excited electronic states were characterized by plotting electron density difference maps (EDDMs). An EDDM is defined simply as difference of the electron density of the excited state and that of the ground state at the same nuclear geometry. Thus, the EDDM shows the redistribution of electron density due to vertical excitation.

All calculations were performed for isolated molecules.

## **SI-2** Electronic structure calculations

## Molecular geometries

We begin the discussion of the simulation results by examining the ground-state equilibrium geometries of the compounds under study, which are shown in **Figure S1**. For all four compounds, the DFT optimizations predict that the phenylene linker (L) projects out of the plane of the acceptor moiety (A).

For compound **4a**, the optimization within the  $C_s$  point group leads to a first-order saddle point on the ground-state potential energy surface (PES). The single imaginary frequency is 7.9 i cm<sup>-1</sup>, and corresponds to an intramolecular rotation of the electron-donating group (D) around the C–N bond which connects it to the the phenylene linker. We decided to nevertheless use the resulting  $C_s$ -symmetric geometry as the basis for the calculation of the electronic excitation spectrum, as the imposition of  $C_s$  symmetry enables the resulting excited electronic states to be classified by symmetry, and also allows a substantial saving of computing time.

For compound **4b**, the optimization within  $C_s$  symmetry likewise leads to a first-order saddle point on the ground-state PES. The imaginary frequency is 28.8 i cm<sup>-1</sup>, and it corresponds to an out-of-plane deformation of the donor moiety.

Unlike the two compounds discussed above, in the case of compound  $4c C_s$  symmetry corresponds to a minimum on the ground-state PES, with no imaginary frequencies.

Lastly, in the case of compound 4d,  $C_s$  symmetry cannot be imposed. For this compound, we located three ground-state conformers, which we label I, II, and III in order of increasing energy. All three conformers correspond to minima on the ground-state PES, and they differ mainly in the conformation of the donor moiety and its orientation with respect to the phenylene linker. Conformers II and III are calculated to be higher in energy by 7.5 kJ/mol and 11.8 kJ/mol, respectively, than conformer I (here, the energy differences include zero-point vibrational energy corrections).



**Figure S1.** Molecular geometries of the compounds under study as optimized at the B3LYP-D3/def2-SVP level of theory. In the case of compounds **4a**, **4b**, and **4c**, the optimizations were performed within  $C_s$  symmetry. The donor, linker, and acceptor moieties are labelled D, L, and A, respectively.

## HOMO and LUMO energy levels

The HOMO and LUMO energy levels of compounds **4a-4d** were calculated at the B3LYP-D3/def2-SVP level of theory. Unlike during the calculation of vertical excitation spectra, the methyl and the *tert*-butyl substituents of compounds **4a** and **4b** were included in the calculations. Moreover, no symmetry constraints were imposed during the calculations. The resulting geometries correspond to true minima, with no imaginary vibrational frequencies. In the case of compound **4d**, when calculating the HOMO and LUMO levels, we only take into account conformer **I**.

**Table S1** compares the calculated HOMO and LUMO levels with the values obtained from electrochemical measurements. For ease of reference, the same data is presented visually

in **Figure S2**. It can be seen that the B3LYP-D3/def2-SVP reproduces the experimental HOMO energies reasonably well. On the other hand, the calculation consistently overestimates the LUMO energies by roughly 0.9 eV.

Table S1. Calculated and experimental HOMO and LUMO energies for compounds 4a-4d.

| Compound  | Calculated (B3LYP-D3/def2-SVP) |                        | Experimental        |                    |  |
|-----------|--------------------------------|------------------------|---------------------|--------------------|--|
|           | $E_{\rm HOMO}$ , eV            | $E_{\text{LUMO}}$ , eV | $E_{\rm HOMO}$ , eV | $E_{ m LUMO}$ , eV |  |
| <b>4a</b> | -5.20                          | -2.21                  | -5.53               | -3.11              |  |
| <b>4b</b> | -5.03                          | -2.22                  | -5.39               | -3.09              |  |
| 4c        | -4.65                          | -2.26                  | -5.24               | -3.06              |  |
| <b>4d</b> | -4.75                          | -2.11                  | -5.06               | -3.08              |  |



Figure S2. Calculated (calc.) and experimental (exp.) HOMO and LUMO energies for compounds 4a-4d.

## Vertical excitation spectra

The calculated vertical excitation spectra of **4a**, **4b**, and **4c** are given in **Table S2**. Accompanying this data, **Figure S3**, **Figure S4** and **Figure S5** show EDDMs of the low-lying excited states of thee compounds.

As can be seen from **Table S2**, the electronic excitation spectra of the compounds under study are fairly complex, with many closely spaced low-lying excited states, and this goes for both the singlet and the triplet states. Furthermore, the structure and ordering of the excited states is sensitive to the nature of the donor moiety. Nevertheless, some generalizations can be made. All three compounds possess a singlet  $\pi\pi^*$ -type excited state of *A*' symmetry at an energy of around 4.0 eV that is localized on the acceptor moiety. The transition to this state carries substantial oscillator strength, and hence it makes a significant contribution to the first photoabsorption band in the range of around 380–420 nm. Furthermore, fluorescence emission from this A'-symmetric singlet  $\pi\pi^*$ -type state is responsible for the experimentally-observed emission band in the range of around 500–650 nm. The electric dipole moment of this state is small and similar in magnitude to that of the singlet ground state, which explains why the emission profile is rather insensitive to solvent polarity.

Slightly higher in energy, at around 4.1 eV, there is a singlet  $n\pi^*$ -type excited state, again of *A*' symmetry, that is also localized on the acceptor moiety. The transition to this latter state carries little oscillator strength. Moreover, among the low-lying singlet excited states of *A*' symmetry, we also find  $\pi\pi^*$ -type excited states that are localized on the donor moiety. Transitions into these states have moderate to large oscillator strengths, and they will contribute to the first photoabsorption band of the given compound.

For compounds **4a** and **4b**, we find a singlet *A*'-symmetric state which involves intramolecular charge transfer (ICT) from the phenylene linker onto the acceptor moiety. Presumably, an analogous  $L \rightarrow ICT$  state also exists in compound **4c**, but it has not been detected in our calculations, because it is not found among the lowest four singlet excited states of *A*' symmetry.

For all three compounds, the four lowest singlet excited states of A" symmetry have low oscillator strengths, meaning that their contribution to the first photoabsorption band is negligible. In all three compounds, the lowest A"-symmetric singlet state corresponds to ICT from the donor moiety onto the acceptor moiety. In the case of **4a**, this D $\rightarrow$ A ICT state is calculated to be fairly high in energy, roughly 0.5 eV above the bright A'-symmetric  $\pi\pi^*$ -type state that is localized on the acceptor moiety. In compounds **4b** and **4c**, on the other hand, the D $\rightarrow$ A ICT state lies close in energy to that  $\pi\pi^*$ -type state. In fact, in the case of compound **4c**, the D $\rightarrow$ A ICT state is calculated to be the lowest from among all singlet excited states. This finding indicates that following the irradiation of the first photoabsorption band, the D $\rightarrow$ A ICT states of compounds **4b** and **4c** may become populated by internal conversion from the lowlying A'-symmetric  $\pi\pi^*$ -type excited states. However, the ICT states cannot exhibit detectable fluorescence emission, as their oscillator are very low. Indeed, the experimentally observed emission spectra show no evidence for fluorescence emission from the ICT states.

The other *A*"-symmetric singlet excited states of **4a**, **4b**, and **4c** lie fairly high in energy relative to the low-lying A'-symmetric  $\pi\pi^*$ -type states, and so they are not expected to play a significant role in these compounds' photophysics.

Moving now on to the triplet states, for all three compounds the lowest triplet excited state is an  $\pi\pi^*$ -type state of *A*" symmetry that is localized on the acceptor moiety. We expect that this state gives rise to the phosphorescence emission of these compounds (if any).

As mentioned previously, we were unable to calculate the electronic excitation spectrum of **4d**. However, due to the fact that **4d** and **4b** are very similar in terms of structure, we expect that their electronic excitation spectra are likewise similar.

**Table S2.** Vertical excitation spectra of compounds **4a**, **4b**, and **4c** as calculated at the SOS-ADC(2)/6-31G(d) level of theory – vertical excitation energies  $\Delta E$  and associated oscillator strengths (f).  $\lambda$  is the photon wavelength corresponding to vertical excitation energy  $\Delta E$ . For the singlet ground state (1 <sup>1</sup>A'), the electric dipole moment was calculated at the SOS-MP2/6-31G(d) level. All calculations were performed at ground-state equilibrium geometries optimized at the B3LYP-D3/def2-SVP level. In the state designations, D denotes the donor moiety, L is the phenylene linker, and A is the acceptor moiety.  $\mu$  is the magnitude of the (orbital-unrelaxed) electric dipole moment of the given state.

| Compound | State                                     | $\Delta E$ , eV | $\lambda$ , nm | f                  | μ, D |
|----------|---|-----------------|----------------|--------------------|------|
| 4a       | 1 <sup>1</sup> <i>A</i> '                 |                 |                |                    | 3.6  |
|          | $2 {}^{1}A' (A \pi \pi^*)$                | 4.047           | 306            | 0.096              | 2.9  |
|          | $3 {}^{1}A' (A n\pi^*)$                   | 4.150           | 299            | 0.014              | 3.9  |
|          | 4 <sup>1</sup> <i>A</i> ' (D ππ*)         | 4.191           | 296            | 0.044              | 5.0  |
|          | 5 ${}^{1}A'$ (L $\rightarrow$ A ICT)      | 4.299           | 288            | 0.016              | 11.5 |
|          | 1 <sup>1</sup> <i>A</i> " (D→A ICT)       | 4.563           | 272            | 9×10 <sup>-5</sup> | 22.0 |
|          | 2 <sup>1</sup> <i>A</i> " (L $\pi\pi^*$ ) | 4.579           | 271            | 0.004              | 3.6  |
|          | 3 <sup>1</sup> <i>A</i> " (Α ππ*)         | 4.694           | 264            | 3×10 <sup>-4</sup> | 3.1  |
|          | 4 ${}^{1}A''$ (A $\pi\pi^*$ )             | 4.757           | 261            | 0.009              | 4.8  |
|          | $1 {}^{3}A' (A n\pi^*)$                   | 3.708           | 334            | 0                  | 3.8  |
|          | 2 <sup>3</sup> <i>A</i> ' (Α ππ*)         | 3.719           | 333            | 0                  | 3.8  |
|          | 3 <sup>3</sup> <i>A</i> ' (D ππ*)         | 3.738           | 332            | 0                  | 3.5  |

|    | 4 <sup>3</sup> <i>A</i> ' (D ππ*)   | 3.922 | 316 | 0                  | 5.8  |
|----|-------------------------------------|-------|-----|--------------------|------|
|    | $1 {}^{3}A'' (A \pi \pi^*)$         | 3.303 | 375 | 0                  | 3.2  |
|    | $2^{3}A'' (A \pi \pi^*)$            | 4.012 | 309 | 0                  | 3.7  |
|    | $3^{3}A'' (A \pi \pi^*)$            | 4.442 | 279 | 0                  | 2.8  |
|    | 4 <sup>3</sup> <i>A</i> " (L ππ*)   | 4.517 | 274 | 0                  | 3.8  |
| 4b | $1  {}^{1}A'$                       |       |     |                    | 3.0  |
|    | 2 <sup>1</sup> <i>A</i> ' (Α ππ*)   | 4.041 | 307 | 0.100              | 2.2  |
|    | $3 {}^{1}A' (A n\pi^*)$             | 4.146 | 299 | 0.020              | 3.2  |
|    | $4 {}^{1}A' (L \rightarrow A ICT)$  | 4.230 | 293 | 0.016              | 11.4 |
|    | 5 <sup>1</sup> <i>A</i> ' (D ππ*)   | 4.394 | 282 | 0.028              | 4.3  |
|    | $1 {}^{1}A'' (D \rightarrow A ICT)$ | 4.050 | 306 | 2×10 <sup>-5</sup> | 26.2 |
|    | 2 <sup>1</sup> <i>A</i> " (L ππ*)   | 4.545 | 273 | 0.005              | 3.1  |
|    | 3 <sup>1</sup> <i>A</i> " (Α ππ*)   | 4.683 | 265 | 3×10 <sup>-4</sup> | 4.2  |
|    | 4 ${}^{1}A''$ (A $\pi\pi^*$ )       | 4.746 | 261 | 0.009              | 4.1  |
|    | $1 {}^{3}A' (A n\pi^*)$             | 3.693 | 336 | 0                  | 3.2  |
|    | $2^{3}A'$ (A n $\pi^*$ )            | 3.712 | 334 | 0                  | 3.1  |
|    | 3 <sup>3</sup> <i>A</i> ' (D ππ*)   | 3.744 | 331 | 0                  | 3.5  |
|    | 4 <sup>3</sup> <i>A</i> ' (L ππ*)   | 4.002 | 310 | 0                  | 3.4  |
|    | $1 {}^{3}A'' (A \pi \pi^*)$         | 3.299 | 376 | 0                  | 3.1  |
|    | $2^{3}A'' (A \pi \pi^*)$            | 4.005 | 310 | 0                  | 2.1  |
|    | $3 {}^{3}A'' (D \rightarrow A ICT)$ | 4.052 | 306 | 0                  | 25.3 |
|    | 4 <sup>3</sup> <i>A</i> " (L ππ*)   | 4.431 | 280 | 0                  | 2.7  |
| 4c | $1  {}^{1}A'$                       |       |     |                    | 4.3  |
|    | 2 <sup>1</sup> <i>A</i> ' (Α ππ*)   | 4.043 | 307 | 0.095              | 3.6  |
|    | 3 <sup>1</sup> <i>A</i> ' (D ππ*)   | 4.103 | 302 | 0.014              | 4.0  |
|    | 4 ${}^{1}A'$ (A n $\pi^*$ )         | 4.146 | 299 | 0.017              | 4.5  |
|    | 5 <sup>1</sup> <i>A</i> ' (D ππ*)   | 4.233 | 293 | 0.123              | 2.6  |
|    | $1 {}^{1}A'' (D \rightarrow A ICT)$ | 3.797 | 327 | 6×10 <sup>-6</sup> | 25.7 |
|    | 2 <sup>1</sup> <i>A</i> " (L ππ*)   | 4.565 | 272 | 0.005              | 4.2  |
|    | $3 {}^{1}A'' (A \pi \pi^*)$         | 4.680 | 265 | 3×10 <sup>-4</sup> | 4.3  |
|    | 4 ${}^{1}A''$ (A $\pi\pi^*$ )       | 4.748 | 261 | 0.009              | 5.5  |
|    | 1 <sup>3</sup> <i>A</i> ' (D ππ*)   | 3.371 | 368 | 0                  | 4.6  |
|    | $2^{3}A' (A n\pi^*)$                | 3.696 | 335 | 0                  | 4.5  |
|    | $3^{3}A'$ (A n $\pi^{*}$ )          | 3.713 | 334 | 0                  | 4.4  |
|    | 4 <sup>3</sup> <i>A</i> ' (L ππ*)   | 4.010 | 309 | 0                  | 4.8  |
|    | $1 {}^{3}A'' (A \pi \pi^*)$         | 3.299 | 376 | 0                  | 3.9  |
|    | $2 {}^{3}A'' (D \rightarrow A ICT)$ | 3.797 | 327 | 0                  | 25.6 |
|    | 3 <sup>3</sup> <i>A</i> " (Α ππ*)   | 4.008 | 309 | 0                  | 4.3  |
|    |                                     |       |     |                    |      |



**Figure S3.** EDDMs of the low-lying excited electronic states of compound **4a**. The EDDMs are plotted in the form of isosurfaces with isovalues of  $\pm 0.002 \text{ e/a}_0^3$ . The red and blue isosurfaces delimit regions in which the electron density is increased and decreased, respectively, relative to the ground state (1 <sup>1</sup>A').



(a)  $2 {}^{1}A' (A \pi \pi^*)$ 



(e) 1  ${}^{1}A''$  (D $\rightarrow$ A ICT)



(b)  $3 {}^{1}A' (A n\pi^*)$ 



(f)  $2 {}^{1}A'' (L \pi \pi^*)$ 



(c)  $4 {}^{1}A'$  (L $\rightarrow$ A ICT)



(d) 5  ${}^{1}A'$  (D  $\pi\pi^*$ )



(h) 4  ${}^{1}A''$  (A  $\pi\pi^*$ )



(i)  $1^{3}A'$  (A n $\pi^{*}$ )



(k)  $3^{3}A'$  (D  $\pi\pi^{*}$ )







(j)  $2^{3}A'$  (A n $\pi^{*}$ )



(m)  $1^{3}A'' (A \pi \pi^{*})$ 



(n)  $2^{3}A'' (A \pi \pi^*)$ 

(o)  $3^{3}A''$  (D $\rightarrow$ A ICT)

(1) 4  ${}^{3}A'$  (L  $\pi\pi^*$ )



(p)  $4^{3}A''$  (L  $\pi\pi^{*}$ )

Figure S4. EDDMs of the low-lying excited electronic states of compound 4b. The EDDMs are plotted in the form of isosurfaces with isovalues of  $\pm 0.002$  e/a<sub>0</sub><sup>3</sup>. The red and blue isosurfaces delimit regions in which the electron density is increased and decreased, respectively, relative to the ground state  $(1 \ ^{1}A')$ .



**Figure S5.** EDDMs of the low-lying excited electronic states of compound **4c**. The EDDMs are plotted in the form of isosurfaces with isovalues of  $\pm 0.002 \text{ e/a}_0^3$ . The red and blue isosurfaces delimit regions in which the electron density is increased and decreased, respectively, relative to the ground state (1 <sup>1</sup>A').

## **SI-3** Synthetic procedures



Scheme S1. The synthetic pathway towards N-PAHs with D-A-D electronic stucture.



## General procedure for the synthesis of 5H-dibenzo[b,f]azepine-10,11-dione (1):

5H-dibenzo[b,f]azepine-10,11-dione (1) was prepared by a modified literature procedure. [21] A 100 mL round-bottomed flask was charged with commercially available oxcarbazepine (1.00 g, 3.96 mmol, 1.0 equiv.) and dry 1,4-dioxane (20 mL). The solution was purged with argon for 10 minutes. Afterwards, SeO<sub>2</sub> (1.08 g, 9.73 mmol, 2.5 equiv.) was added to the flask. The reaction mixture was refluxed (105°C)

overnight with reflux condenser under argon atmosphere. After cooling it to the room temperature, the red precipitate has been filtrated carefully to avoid transferring selenium residues to the funnel. The subsequent recrystallization from DCM/MeOH affording pure compound **1** (707 mg, 80%) as an orange solid. <sup>1</sup>H NMR (400 MHz, 300K, DMSO-*d*<sub>6</sub>)  $\delta$  10.76 (s, 1H), 7.85 (dd, *J* = 8.1, 1.6 Hz, 2H), 7.70 (ddd, *J* = 8.5, 6.9, 1.7 Hz, 2H), 7.56 (dd, *J* = 8.5, 1.0 Hz, 2H), 7.20 (ddd, *J* = 7.9, 6.8, 1.1 Hz, 2H). <sup>13</sup>C NMR (101 MHz, 300K, DMSO)  $\delta$  188.1, 140.8, 134.6, 130.0, 121.7, 120.2, 119.9. The NMR data are in accordance with those reported in the literature. [22]



## General procedure for the synthesis of 2:

A Schlenk tube was charged with compound 1 (500 mg, 2.24 mmol, 1.0 equiv.) and 4,5-dimethyl-1,2-phenylenediamine (305 mg, 2.24 mmol, 1.0 equiv.), following by glacial acetic acid (40 mL) and anhydrous ethyl alcohol 99.8% (40 mL). The mixture was argon purged for 20 minutes and reaction was stirred overnight at 120°C under inert atmosphere. After cooling the mixture, solvents were removed under reduced pressure. The crude mixture was purified by a column chromatography separation on silica gel (DCM/acetone, 49:1) affording compound 2 (300 mg, 41%) as a yellow solid. <sup>1</sup>H NMR (400 MHz, 300K, Chloroform-*d*)  $\delta$  8.09 (dd, *J* = 7.8, 1.6 Hz, 2H), 7.90 (s, 2H), 7.32 (td, *J* = 7.6, 1.6 Hz, 2H), 7.20 (td, *J* = 7.5, 1.2

Hz, 2H), 6.91 (dd, *J* = 7.9, 1.2 Hz, 2H), 5.40 (s, 1H), 2.51 (s, 6H). <sup>13</sup>C NMR (126 MHz, 300K, CDCl<sub>3</sub>) δ 151.7, 150.7, 140.9, 140.6, 132.0, 130.6, 130.2, 128.4, 124.3, 119.8, 20.6.



## General procedure for the synthesis of 3:

Compound **2** (150 mg, 0.46 mmol, 1.0 equiv.), 1-chloro-4iodobenzene (120 mg, 0.50 mmol, 1.1 equiv.) and NaO*tBu* (88 mg, 0.92 mmol, 2.0 equiv.) were added to an oven-dried and argon flushed pressure tube equipped with magnetic stir bar, following by dry toluene (10 mL). The mixture was purged with argon for 10 minutes. Afterwards, Pd(OAc)<sub>2</sub> (7 mg, 0.03 mmol, 0.06 equiv.) and P(*t*Bu)<sub>3</sub>HBF<sub>4</sub> (17 mg, 0.06 mmol, 0.12 equiv.) were added at once and the reaction mixture was purged with argon an additional two minutes and the tube was tightly sealed. The reaction mixture was refluxed (105°C) overnight under inert atmosphere. After cooling the reaction mixture to the room temperature, toluene was removed under reduced pressure. The product was dissolved in 30 mL of DCM, water was added and aqueous phase was extracted 3 times

with DCM. The organic layers were combined and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Organic solvents were removed under vacuum and the crude mixture was purified by a flash column chromatography separation on silica gel (hexane/DCM, 1:1) affording compound **3** (150 mg, 75%) as a yellow solid. <sup>1</sup>H NMR (500 MHz, 300K, Chloroform-*d*)  $\delta$  8.20 (dt, *J* = 7.6, 1.3 Hz, 2H), 7.94 – 7.91 (m, 2H), 7.62 – 7.57 (m, 4H), 7.55 – 7.51 (m, 2H), 6.87 – 6.83 (m, 2H), 6.43 (m, 2H), 2.51 (s, 6H). <sup>13</sup>C NMR (126 MHz, 300K, CDCl<sub>3</sub>)  $\delta$  149.8, 146.7, 146.2, 141.2, 140.7, 137.8, 132.7, 131.2, 129.1, 128.7, 128.5, 128.2, 123.2, 113.5, 20.6.



## General procedure for the synthesis of 4a-d:

Compound **3** (66 mg, 0.152 mmol, 1.00 equiv.), appropriate amine donor (0.167 mmol, 1.10 equiv.) and NaO*tBu* (16 mg, 0.16 mmol, 1.05 equiv.) were added to an oven-dried and argon flushed pressure tube equipped with magnetic stir bar, following by dry p-xylene (3 mL). The mixture was purged with argon for 10 minutes. Afterwards,  $Pd_2(dba)_3$  (6 mg, 0.011 mmol, 0.075 equiv.) and XPhos (13 mg, 0.023 mmol, 0.15 equiv.) were added at once and the reaction mixture was purged with argon an additional two minutes and the tube was tightly sealed. The reaction mixture was heated (140°C) overnight (**4a**, **4d**) or 3 days (**4b**, **4c**) under inert atmosphere. After cooling the reaction mixture to the room temperature, p-xylene was removed under reduced pressure. The product was dissolved in 20 mL of DCM, water was added and aqueous phase was extracted 3 times with DCM. The organic layers

were combined and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Organic solvents were removed under vacuum and the crude mixture was purified by a column chromatography separation on silica gel (hexane/DCM, 3:2). The subsequent recrystallization from DCM/MeOH affording pure compounds **4a-4d**.



4a, Yellow solid, yield: 63%.

<sup>1</sup>H NMR (600 MHz, 300K, Chloroform-*d*)  $\delta$  8.25 (dd, *J* = 7.8, 1.6 Hz, 2H), 8.05 (dd, *J* = 2.0, 0.6 Hz, 2H), 7.98 (s, 2H), 7.73 (m, 2H), 7.65 (td, *J* = 7.6, 1.6 Hz, 2H), 7.56 (td, *J* = 7.6, 1.3 Hz, 2H), 7.31 (dd, *J* = 8.6, 2.0 Hz, 2H), 7.11 – 7.05 (m, 4H), 6.71 (d, *J* = 9.0 Hz, 2H), 2.57 – 2.52 (s, 6H), 1.41 (s, 18H).

<sup>13</sup>C NMR (151 MHz, 300K, cdcl<sub>3</sub>) δ 150.0, 146.8, 146.4, 142.3, 141.2, 140.8, 139.8, 137.7, 132.7, 131.2, 129.1, 128.6, 128.5, 128.2, 127.5, 123.3, 123.0, 116.1, 113.1, 109.3, 34.8, 32.2, 20.6. HRMS (EI) calcd for C<sub>48</sub>H<sub>44</sub>N<sub>4</sub>: 676.3566 [M]+, found: 676.3562; IR (KBr)  $\tilde{v}$ =3040(w), 2952(m), 2863(m), 1746(w), 1598(w), 1509(s), 1488(s), 1453(s), 1392(w), 1348(m), 1317(s), 1294(s), 1261 (m), 1234(m), 1208(m), 1156(w), 1103(w), 1056(m), 1027(m), 973(w), 872(m), 810(m), 761(m), 610(m), 530(m) cm<sup>-1</sup>;



4b, Yellow solid, yield: 36%.

<sup>1</sup>H NMR (600 MHz, 300K, Chloroform-*d*)  $\delta$  8.23 (dd, *J* = 7.8, 1.6 Hz, 2H), 7.98 (s, 2H), 7.74 (dd, *J* = 7.9, 1.2 Hz, 2H), 7.64 (td, *J* = 7.6, 1.6 Hz, 2H), 7.55 (td, *J* = 7.5, 1.3 Hz, 2H), 7.34 (dd, *J* = 7.7, 1.6 Hz, 2H), 6.86 – 6.79 (m, 4H), 6.77 – 6.72 (m, 4H), 6.06 (dd, *J* = 8.2, 1.3 Hz, 2H), 2.55 (s, 6H), 1.59 (s, 6H).

<sup>13</sup>C NMR (151 MHz, 300K, cdcl<sub>3</sub>) δ 150.1, 147.6, 146.7, 141.4, 141.2, 140.7, 137.6, 132.7, 131.5, 131.3, 131.2, 129.9, 129.0, 128.5, 128.1, 126.2, 125.0, 120.2, 114.5, 114.2, 36.0, 31.3, 20.6.

HRMS (EI) calcd for  $C_{43}H_{34}N_4$ : 606.2783 [M]+, found: 606.2770; IR (KBr)  $\tilde{v}$ =3061(w), 2968(w), 2853(w), 1651(w), 1611(w), 1589(m), 1545(w), 1508(s), 1477(s), 1447(s), 1333(s), 1317(s), 1269(m), 1207(m), 1169(w), 1113(w), 1063(m), 1024(m), 972(w), 870(m), 831(w), 743(s), 621(m), 555(m), 527(m), 434(w) cm<sup>-1</sup>;



4c, Orange solid, yield: 32%.

<sup>1</sup>H NMR (500 MHz, 300K, Chloroform-*d*)  $\delta$  8.22 (dd, *J* = 7.8, 1.6 Hz, 2H), 7.97 (s, 2H), 7.69 (dd, *J* = 7.9, 1.3 Hz, 2H), 7.63 (td, *J* = 7.6, 1.6 Hz, 2H), 7.55 (td, *J* = 7.5, 1.4 Hz, 2H), 6.84 (d, *J* = 9.0 Hz, 2H), 6.70 (d, *J* = 9.0 Hz, 2H), 6.56 (dd, *J* = 7.8, 1.6 Hz, 2H), 6.51 (td, *J* = 7.6, 1.5 Hz, 2H), 6.39 (td, *J* = 7.7, 1.6 Hz, 2H), 5.70 (dd, *J* = 8.0, 1.5 Hz, 2H), 2.54 (s, 6H).

<sup>13</sup>C NMR (126 MHz, 300K, cdcl<sub>3</sub>) δ 150.0, 147.7, 146.5, 144.0, 141.2, 140.7, 137.6, 135.0, 132.7, 131.2, 131.0, 129.0, 128.9, 128.5, 128.2, 123.2, 120.9, 115.2, 114.5, 113.3, 20.6.

HRMS (EI) calcd for C<sub>40</sub>H<sub>28</sub>N<sub>4</sub>O: 580.2263 [M]+, found: 580.2256; IR (KBr)  $\tilde{\nu}$ =3061(w), 2920(w), 2851(w), 1721(w), 1655(w), 1626(w), 1591(m), 1545(w), 1506(s), 1483(s), 1462(m), 1325(s), 1314(s), 1267(s), 1207(m), 1115(m), 1063(m), 1026(m), 972(w), 955(w), 920(w), 866(m), 770(m), 741(s), 615(w), 517(w), 521(m), 436(w) cm<sup>-1</sup>;



4d, Yellow solid, yield: 33%.

<sup>1</sup>H NMR (500 MHz, 300K, Chloroform-*d*)  $\delta$  8.12 (dd, *J* = 7.7, 1.6 Hz, 2H), 7.93 (s, 2H), 7.60 (dd, *J* = 8.0, 1.3 Hz, 2H), 7.51 (td, *J* = 7.6, 1.6 Hz, 2H), 7.43 (td, *J* = 7.5, 1.3 Hz, 2H), 7.25 – 7.21 (m, 2H), 7.14 – 7.04 (m, 6H), 6.46 – 6.41 (m, 2H), 6.28 (m, 2H), 2.84 (s, 4H), 2.53 (s, 6H).

<sup>13</sup>C NMR (126 MHz, 300K, cdcl<sub>3</sub>) δ 150.6, 147.5, 144.1, 142.0, 140.8, 140.6, 140.0, 138.4, 137.8, 132.4, 130.8, 130.8, 130.1, 129.0, 128.5, 127.4, 126.9, 126.5, 114.2, 113.1, 31.2, 20.6.

HRMS (EI) calcd for  $C_{42}H_{32}N_4$ : 592.2627 [M]+, found: 592.2621; IR (KBr)  $\tilde{v}$ =3447(m), 2920(w), 1657(w), 1545(w), 1509(s), 1449(m), 1344(m), 1300(m), 1269(s), 1209(m), 1157(w), 1105(w), 1063(m), 1026(m), 972(w), 870(m), 810(m), 762(m), 548(w), 505(w) cm<sup>-1</sup>;

#### SI-4 Steady-state characterisation



**Figure S6.** UV-vis absorption and PL spectra of **4a-d** (c 10–5 M) diluted solutions in dichloromethane, tetrahydrofuran, and toluene solvents.



Figure S7. PL spectra of 4a-d in solid CBP and Zeonex matrix.

## **SI-5** Photophysics



**Figure S8.** Time-Resolved Spectra of compounds **4a-d** in Zeonex matrix (a, c, e, g), the energies correspond to the maximum emission peaks. Intensity vs delay time measurement decays (b, d, f, h).

| Commonweak | λ <sub>em</sub> , | Host   | PLQY           | τ <sub>ΡF</sub> , | τ <sub>DF</sub> , | DF/PF <sup>e</sup> | Eaf   | S1              | Τ1,             | ΔEsτ,           |
|------------|-------------------|--------|----------------|-------------------|-------------------|--------------------|-------|-----------------|-----------------|-----------------|
| Compound   | nmª               |        | % <sup>b</sup> | nsc               | μs <sup>d</sup>   |                    |       | eV <sup>g</sup> | eV <sup>g</sup> | eV <sup>h</sup> |
| 4a         | 513               | Zeonex | 12.1           | 8.52+-0.13        | 1.51+-0.65        | 32.36              | 0.028 | 2.43            | 2.43            | 0.00            |
| 4a         | 537               | СВР    | 25.6           | 12.48+-0.36       | 19.02+-1.15       | 4.57               | 0.017 | 2.30            | 2.25            | 0.05            |
| 4b         | 504               | Zeonex | 6.6            | 15.21+-0.33       | 2.76+-0.20        | 17.00              | 0.034 | 2.46            | 2.53            | -0.07           |
| 4b         | 543               | СВР    | 23.2           | 14.80+-0.49       | 29.9+-3           | 2.02               | 0.018 | 2.31            | 2.19            | 0.12            |
| 4c         | 535               | Zeonex | 14.4           | 15.41+-0.74       | 51.22+-7.1        | 10.52              | 0.018 | 2.35            | 2.35            | 0.00            |
| 4c         | 556               | CBP    | 34             | 27.36+-1.6        | 32.7+-3.1         | 1.98               | 0.011 | 2.24            | 2.21            | 0.03            |
| 4d         | 590               | Zeonex | 2.6            | 16.62+-0.48       | 2.6+-0.26         | 0.30               | 0.009 | 2.10            | 2.33            | -0.23           |
| 4d         | 571               | CBP    | 10.5           | 10.07+-0.22       | 4.14+-0.40        | 0.56               | 0.010 | 2.25            | 2.39            | -0.14           |

<sup>a</sup> Photoluminescence maximum; <sup>b</sup> Photoluminescence quantum yield; <sup>c</sup> Prompt fluorescence lifetime in the host; <sup>d</sup> Delayed emission lifetime in the host; <sup>e</sup> Delayed fluorescence (DF) to prompt fluorescence (PF) ratio in the host; <sup>f</sup> Activation energy of the triplet to singlet transfer <sup>g</sup> Singlet and triplet energy in host. Error ± 0.03 eV; <sup>h</sup> Singlet-triplet energy splitting in Zeonex. Error ± 0.05 eV.

## SI-6 Cyclic voltammetry



**Figure S9.** CV of 1 mM concentration of compounds **4a-d** in 0.1 M Bu<sub>4</sub>NBF<sub>4</sub> in DCM electrolyte at the scan rate of 50 mV/s.

## SI-7 X-Ray crystallography analysis

The crystals selected for X-ray analysis had shapes, respectively, for compound **4a** with the formula  $C_{99}H_{88}Cl_2N_8$  - yellow needles with dimensions of 0.172 mm x 0.209 mm x 0.335 mm, for compound **4b** with the formula  $C_{43}H_{34}Cl_2N_4$  - yellow prisms with dimensions of 0.168 x 0.255 x 0.270 mm and for compound **4d** with the formula  $C_{42}H_{32}N_4$  - fluorescent colorless-yellow prisms with dimensions of 0.147 x 0.244 x 0.492 mm.

Crystal crystallographic data for all samples were collected at room temperature (T = 296(2) K) using a Bruker X8 APEXII diffractometer with Cu-K $\alpha$  radiation ( $\lambda$  = 1.54178 Å). Frames were integrated with the Bruker SAINT [23] software package using a narrow-frame algorithm. The structures ware solved and refined using the Bruker SHELXTL Software Package [24, 25]. All obtained data were corrected for absorption effects using the face-indexed numerical method (SADABS) [26]. Same hydrogens were found from the difference electron density maps and refined with an anisotropic thermal motion model. Other hydrogen atoms were placed in calculated positions and refined as riding on their parent atoms with U<sub>iso</sub> = 1.2 Ueq. The structure was solved by direct methods SHELXS-2014 [27] and refined with full-matrix least-squares calculations on  $F^2$  using SHELX-2014 [27]. All non-hydrogen atoms were refined anisotropically.

Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre, 12 Union Road, 129 Cambridge CB2 1EZ, UK, and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number.

The details concerning the crystal data and structural parameters of **4a**, **4b** and **4d** are collected in **Table S4**.

|                        | <b>4</b> a            | <b>4b</b>             | <b>4d</b>         |
|------------------------|-----------------------|-----------------------|-------------------|
| Identification code    | WDE0049_10B_A         | WDE0056_10B_A         | WDE0053_10B       |
| Chemical formula       | $C_{99}H_{88}Cl_2N_8$ | $C_{43}H_{34}Cl_2N_4$ | $C_{42}H_{32}N_4$ |
| Formula weight [g/mol] | 1460.67 g/mol         | 677.64                | 592.71            |
| CCDC Number            | 2216025               | 2216027               | 2216026           |
|                        | 0.172 x 0.209 x       | 0.168 x 0.255 x       | 0.147 x 0.244 x   |
|                        | 0.335                 | 0.270                 | 0.492             |
| Cwystal babit          | Vallow needle         | Vallow prism          | Colourless-yellow |
| Crystal habit          | renow needle          | r enow prism          | prism             |
| Crystal system         | Monoclinic            | Monoclinic            | Triclinic         |
| Space group            | $C2_1/c$              | $P2_1/n$              | ΡĪ                |

Table S4. Data collection and structure refinement parameters for 4a, 4b and 4d.

| Unit cell dimensions              |                          |                              |                    |
|-----------------------------------|--------------------------|------------------------------|--------------------|
| <i>a</i> [Å]                      | 27.4329(5)               | 12.7869(3)                   | 10.7776(3)         |
| <b>b</b> [Å]                      | 14.3395(2)               | 11.7310(3)                   |                    |
|                                   | 24.0718(4)               | 18.9250(4)                   | 13.5047(3)         |
| a [°]                             | 90                       | 90                           | 83.888(2)          |
| β <sup>[°]</sup>                  | 122.5130(10)             | 100.7860(10)                 | 74.717(2)          |
| <b>2</b> [°]                      | 90                       | 90                           | 67.2760(10)        |
| <b>Volume</b> [Å <sup>3</sup> ]   | 7985.1(2)                | 3476.70(13)                  | 1519.17(7)         |
| Ζ                                 | 4                        | 4                            | 2                  |
| Density (calculated)              | 1 215                    | 1 205                        | 1 206              |
| [g/cm <sup>3</sup> ]              | 1.213                    | 1.295                        | 1.290              |
| Absorption coefficient            | 1 1/3                    | 1 963                        | 0 591              |
| [mm <sup>-1</sup> ]               | 1.145                    | 1.905                        | 0.391              |
| <b>F(000)</b>                     | 3088                     | 1416                         | 624                |
|                                   |                          |                              |                    |
| Theta range [°]                   | 3.63 to 68.59            | 3.85 to 68.43                | 3.39 to 70.35      |
|                                   | -32<=h<=30, -            | $-15 \le h \le 15$           | $-12 \le h \le 12$ |
| Index ranges                      | 17<=k<=17, -             | $-17 \le k \le 17$           | $-14 \le k \le 13$ |
|                                   | 26<=l<=29                | $-21 \le 1 \le 22$           | $-16 \le l \le 15$ |
| <b>Reflections collected</b>      | 54101                    | 50145                        | 24599              |
| Indopendent reflections           | 7329 (R <sub>int</sub> = | $6382 (R_{int} =$            | $5269 (R_{int} =$  |
| independent reflections           | 0.0777)                  | 0.0813)                      | 0.0655)            |
| Coverage of independent           | 00.5%                    | 00.8.0/                      | 00.0.0/            |
| reflections                       | 99.3%                    | 99.8 %                       | 90.9 %             |
| Absorption correction             | numerical                | numerical                    | numerical          |
| Max. and min.                     | 0.8280 and 0.7010        | 0.7340 and 0.6190            | 0.0180 and 0.7600  |
| transmission                      | 0.0200 and 0.7010        | 0.7540 and 0.0190            | 0.9180 and 0.7000  |
| Structure solution                |                          | direct methods               |                    |
| technique                         |                          | difect methods               |                    |
| Structure solution                | SHEI                     | XI 2014 (Sheldrick           | 2014               |
| program                           | SHEL                     | AL-2014 (Sheldher,           | 2014)              |
| Refinement method                 | Full-                    | matrix least-squares of      | $5n F^2$           |
| Refinement program                | SHEL                     | XL-2014 (Sheldrick,          | 2014)              |
| Function minimized                |                          | $\Sigma w (F_o^2 - F_c^2)^2$ |                    |
| Data / restraints /               | 7329 / 0 / 513           | 6382/0/455                   | 5269/0/501         |
| parameters                        | 1527101515               | 0302/0/+33                   | 52070/501          |
| Goodness-of-fit on F <sup>2</sup> | 0.963                    | 1.046                        | 1.038              |
| $\Delta/\sigma_{\rm max}$         | 0.001                    | -                            | -                  |
| Final R indices                   | 4991 data; I>2σ(I)       | 4140 data; I>2σ(I)           | 3130 data; I>2σ(I) |
| <b>R</b> 1,                       | 0.0830,                  | 0.0822,                      | 0.0477,            |
| wR <sub>2</sub>                   | 0.2192                   | 0.2429                       | 0.1092             |
| R indices (all data):             | $R_1 = 0.1135,$          | $R_1 = 0.1178,$              | $R_1 = 0.1046,$    |
| K multes (an uala):               | $wR_2 = 0.2460$          | $wR_2 = 0.2429$              | $wR_2 = 0.1428$    |

| Weighting scheme   | $w=1/[\sigma^{2}(F_{o}^{2})+$ +(0.1178P) <sup>2</sup> +<br>+18.2544P] | $w=1/[\sigma^{2}(F_{o}^{2})+$ +(0.1597P) <sup>2</sup> + +2.2434P] where P=(F_{o}^{2}+2F_{c}^{2})/3 | $    w=1/[\sigma^2(F_o{}^2)+ \\ +(0.0703P)^2] $ |
|--|---|--|---|
| <b>Extinction coefficient</b>                            | 0.0001(0)   | 0.0005(3)  | -   |
| Largest diff. peak and                                   | 0.658 and   | 0.801 and  | 0.277 and                                       |
| hole [eÅ <sup>-3</sup> ]                                 | -0.942  | -0.844   | -0.257  |
| <b>R.M.S. deviation from</b><br>mean [eÅ <sup>-3</sup> ] | 0.061   | 0.065  | 0.054   |



Figure S10. View of solved structures showing the v-shape created by the compound in the crystal.



Figure S11. An insight to the packing behavior of dyes 4a and 4b, respectively.

SI-8 NMR spectra of synthesized compounds



Figure S12. <sup>1</sup>H NMR spectrum of 2 (400 MHz, 300K, Chloroform-*d*).



<sup>50</sup> 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -4 **Figure S13.** <sup>13</sup>C NMR spectrum of **2** (126 MHz, 300K, CDCl<sub>3</sub>).





<sup>230</sup> <sup>220</sup> <sup>210</sup> <sup>200</sup> <sup>190</sup> <sup>180</sup> <sup>170</sup> <sup>160</sup> <sup>150</sup> <sup>140</sup> <sup>130</sup> <sup>120</sup> <sup>110</sup> <sup>100</sup> <sup>90</sup> <sup>80</sup> <sup>70</sup> <sup>60</sup> <sup>50</sup> <sup>40</sup> <sup>30</sup> <sup>20</sup> <sup>10</sup> <sup>0</sup> <sup>-10</sup> <sup>10</sup> <sup>f1 (ppm)</sup> **Figure S17.** <sup>13</sup>C NMR spectrum of **4a** (151 MHz, 300K, CDCl<sub>3</sub>).





<sup>230</sup> <sup>220</sup> <sup>210</sup> <sup>200</sup> <sup>190</sup> <sup>180</sup> <sup>170</sup> <sup>160</sup> <sup>150</sup> <sup>140</sup> <sup>130</sup> <sup>120</sup> <sup>110</sup> <sup>100</sup> <sup>90</sup> <sup>80</sup> <sup>70</sup> <sup>60</sup> <sup>50</sup> <sup>40</sup> <sup>30</sup> <sup>20</sup> <sup>10</sup> <sup>0</sup> <sup>-10</sup> <sup>10</sup> <sup>Fi</sup> <sup>(ppm)</sup> Figure S19. <sup>13</sup>C NMR spectrum of **4b** (151 MHz, 300K, CDCl<sub>3</sub>).





<sup>50</sup> 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -4 **Figure S21.** <sup>13</sup>C NMR spectrum of **4c** (126 MHz, 300K, CDCl<sub>3</sub>).



<sup>50</sup> 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -4 **Figure S23.** <sup>13</sup>C NMR spectrum of **4d** (126 MHz, 300K, CDCl<sub>3</sub>).

## **SI-9 References**

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