**Electronic supporting information** 

# Revealing Resonance Effects and Intramolecular Dipole Interactions in the Positional Isomers of Benzonitrile-Core Thermally Activated Delayed Fluorescence Materials

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### **S1. Experimental Procedures**

### Materials:

All reagents were purchased from Sigma-Aldrich and used without further purification unless otherwise stated.

### Instrumental and Analytical Techniques:

Nuclear magnetic resonance (NMR) spectra were recorded using a Bruker Advance (III)-400 (<sup>1</sup>H 400.130 MHz and <sup>13</sup>C 100.613 MHz), Varian Inova-500 (<sup>1</sup>H 500.130 MHz and <sup>13</sup>C 125.758 MHz), Varian VNMRS-600 (<sup>1</sup>H 600.130 MHz and <sup>13</sup>C 150.903 MHz) or a Varian VNMRS-700 (1H 700.130 MHz and 13C 176.048 MHz) spectrometer, at a constant temperature of 298 K unless otherwise stated. For variable-temperature (VT) measurements, operating temperatures were calibrated using an internal calibration solution of MeOH and glycerol. Chemical shifts ( $\delta$ ) are reported in parts per million (ppm) relative to the signals corresponding to residual non-deuterated solvents [CD<sub>2</sub>Cl<sub>2</sub>:  $\delta = 5.32$  or 54.00]. Coupling constants (J) are reported in Hertz (Hz). <sup>13</sup>C NMR Experiments were proton-decoupled unless otherwise stated. Assignments of <sup>1</sup>H and <sup>13</sup>C NMR signals were accomplished by twodimensional NMR spectroscopy (COSY, NOESY, HSQC, HMBC). NMR spectra were processed using MestReNova version 11. Data are reported as follows: chemical shift; multiplicity; coupling constants; integral and assignment. Low-resolution mass spectrometry (MS) were performed using a Waters Xevo QTOF equipped with an Atmospheric Solids Analysis Probe (ASAP). High-resolution ASAP (HR-ASAP) mass spectra were measured using a Waters LCT Premier XE high resolution, accurate mass UPLC ES MS (also with ASAP ion source). Elemental analysis data were obtained on a EuroEA Elemental Analyser. TGA was performed on a Metter TGA/SDTA851e/LF/1100 apparatus at a heating rate of 20 °C/min under a nitrogen atmosphere. DSC measurements were done on a DSC Q 100 TA Instrument at a heating rate of 10 °C/min under a nitrogen atmosphere. Melting points (M.P.) of the prepared compounds were estimated using Electrothermal Melt-Temp apparatus. Cyclic voltammetry (CV) measurements were carried out with a glassy carbon working electrode in a three-electrode cell using a  $\mu$ -Autolab Type III (EcoChemie, Netherlands) potentiostat. Platinum wire and Ag/AgNO<sub>3</sub> (0.01 mol/L in acetonitrile) were used as counter and reference electrodes, respectively, and Bu<sub>4</sub>NBF<sub>6</sub> in dichloromethane (0.1 M) was used as electrolyte. The data were collected using GPES (General Purpose Electrochemical System) software. Electrochemical measurements were conducted at room temperature at a potential rate of 100 mV/s. The reference electrode was calibrated versus ferrocene/ferrocenium redox couple. The solid-state ionisation potential energy  $(I_p^{CV})$  was estimated from the onset oxidation potential by using the relationship  $I_p^{CV} = 4.8 + E_{ox}$ , where the potential is related to that of ferrocenium/ferrocene. The electron affinity (EACV) values were obtained from the reduction potential using the approximation  $EA^{CV} = 4.8 + E_{red}$ . The theoretical calculations were carried out using the Gaussian 09 quantum chemical package.<sup>1</sup> Full geometry optimisations of the compounds in their electronic ground state were performed with density functional theory method  $(DFT)^2$  using the BMK<sup>3</sup> functional with the 6-31G(d) basis set in vacuum. The excited-state properties of the molecules were calculated by the means of timedependent DFT (TD-DFT)<sup>4-6</sup> and TDA-DFT<sup>7,8</sup> calculations employing 6-31G(d) basis set in vacuum. The amount of charge (q) transferred from donor to acceptor in the excited state was calculated using the methodology reported elsewhere.<sup>9</sup> The orbital compositional analysis was performed with Multiwfn software.<sup>10</sup> Steady-state absorbance measurements were

conducted using a UV-3600 Shimadzu spectrophotometer and photoluminescence measurements were conducted using a Jobin Yvon Horiba Fluoromax 3. Emission spectra were calibrated for detector efficiency using company supplied instrument specific calibration files. Time-resolved photophysical measurements have been described elsewhere.<sup>11</sup> The excitation source for all temperature-dependent/time-resolved measurements was a nitrogen laser (337 nm) ((LTB-MNL 100, Lasertechnik Berlin) with spectra obtained on a gated intensified charge-coupled device (iCCD) camera (Stanford Computer Optics) at differing delay times. Power-dependent measurements were performed using the same laser source with delayed emission intensity measured as a function of laser fluence between ~0.2-80 µJ. Solid-state samples were prepared on clean quartz substrates prepared as a 1% w/w ratio in Zeonex<sup>®</sup> or a 10% w/w ratio in DPEPO, dropcast from toluene on a hotplate until dry. PLQYs were measured using a calibrated Horiba Quanta- $\Phi$ integrating sphere coupled to a Fluorolog3 spectrometer using 380 nm excitation. Data was processed using the included Fluoracle software. The X-ray single-crystal diffraction data for *meta-2* and *para-3* were collected at 120.0(2) K using  $\lambda$ MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å) on a Bruker D8Venture (Photon100 CMOS detector, IµS-microsource, focusing mirrors) diffractometer and for compound ortho-1 on an Agilent XCalibur (Sapphire-3 CCD detector, fine-focus sealed tube, graphite monochromator) diffractometer, both equipped with a Cryostream (Oxford Cryosystems) open-flow nitrogen cryostats. 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>12</sup> and SHELXT<sup>13</sup> software. All non-hydrogen atoms were refined anisotropically, hydrogen atoms were placed into calculated positions and refined in riding mode. Crystal data and parameters of refinement are listed in Table S1. Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 1917139-1917141.

### **S2. Synthetic Procedures**

### General procedure for diazotiation-iodination reaction<sup>14</sup>

The corresponding amine (2.00 g, 16.9 mmol) in 20 mL of acetone was treated with 10 mL of concentrated HCl at room temperature. The solution was cooled to 0 °C and treated dropwise with NaNO<sub>2</sub> (1.51 g, 22.0 mmol) dissolved in 5 mL of water. The solution was stirred at 0 °C for 2 h and then treated with KI (8.41 g, 50.7 mmol) in 15 mL of water. After 6 h, the solution was quenched with 100 mL of the saturated aqueous solution of Na<sub>2</sub>SO<sub>3</sub> and extracted with diethyl ether ( $3 \times 70$  mL). The combined organic extracts were washed with brine (100 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and the solvent was removed under reduced pressure. The crude residue was purified by flash column chromatography using a 1:9 ratio of ethyl acetate/hexanes to give the desired iodide.

2-Iodobenzonitrile (S1a) M.P. 53 – 55 °C (lit.<sup>15</sup> 54 – 55 °C), 3-iodobenzonitrile (S1b) M.P. 40 - 42 °C (lit.<sup>16</sup> 39 – 40 °C) and 4-iodobenzonitrile (S1c) M.P. 121 - 123 °C (lit.<sup>16</sup> 122 – 124 °C) were prepared according the literature procedures.<sup>16,17</sup>

### General procedure for Buchwald-Hartwig amination reaction<sup>18,17</sup>

2,7-Di-*tert*-butyl-9,9-dimethyl-9,10-dihydroacridine (1.00 g, mmol) and 3.11 the corresponding iodobenzonitrile (0.78 g, 3.42 mmol) were placed in a dry Schlenk reactor and the flask was deaerated then 10 mL of anhydrous toluene was added under an argon atmosphere. t-BuONa (0.89 g, 9.33 mmol) was added and reaction mixture was deaerated. 1,1'-Bis(diphenylphosphino)ferrocene (dppf) (0.17 g, 0.31 mmol) and Pd(OAc)<sub>2</sub> (0.07 g, 0.31 mmol) were then added. The reaction mixture was deaerated again and heated to 115 °C. After 24 h, the reaction mixture was cooled to the room temperature, diluted with water and extracted with ethyl acetate (3  $\times$  100 mL). The combined organic extracts was dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under reduced pressure. The crude residue was purified by silica gel column chromatography, using a 5:1 ratio of hexanes and toluene. The solvent was evaporated and the residue was recrystallised from a 1:4 dichloromethane and isopropanol mixture to yield the desired product.

### 2-(2,7-Di-tert-butyl-9,9-dimethylacridin-10(9H)-yl)benzonitrile (ortho-1)



The title compound was obtained from **S1a** (0.78 g, 3.42 mmol) as off-white crystals (0.87 g, 2.06 mmol, 66%). M.P. 238 – 240 °C (DSC 242 °C). <sup>1</sup>H NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  7.96 (dd, *J* = 7.8, 1.5 Hz, 1H, H<sub>3</sub>), 7.90 (td, *J* = 7.8, 1.6 Hz, 1H, H<sub>4</sub>), 7.68 (td, *J* = 7.7, 1.2 Hz, 1H, H<sub>5</sub>), 7.49 (dd, *J* = 8.0, 1.1 Hz, 1H, H<sub>6</sub>), 7.47 (d, *J* = 2.2 Hz, 2H, H<sub>14</sub>), 6.97 (dd, *J* = 8.6, 2.3 Hz, 2H, H<sub>10</sub>), 5.98 (d, *J* = 8.5 Hz, 2H, H<sub>9</sub>), 1.75 (s, 6H, H<sub>17</sub>), 1.36 (s, 18H, H<sub>13</sub>). <sup>13</sup>C NMR (151 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  145.2 (C<sub>2</sub> or C<sub>1</sub>), 144.1 (C<sub>11</sub>), 138.2 (C<sub>8</sub>), 135.6 (C<sub>3</sub>), 135.2 (C<sub>4</sub>), 134.0

(C<sub>6</sub>), 130.2 (C<sub>15</sub>), 129.2 (C<sub>5</sub>), 124.1 (C<sub>10</sub>), 123.0 (C<sub>14</sub>), 117.3 (C<sub>7</sub>), 116.3 (C<sub>2</sub> or C<sub>1</sub>), 113.4 (C<sub>9</sub>), 37.0 (C<sub>16</sub>), 34.6 (C1<sub>2</sub>), 32.1 (C<sub>17</sub> and C<sub>13</sub>). Elemental analysis found: C, 85.28; H, 8.13; N, 6.59 %; molecular formula  $C_{30}H_{34}N_2$  requires: C, 85.26; H, 8.11; N, 6.63 %. HRMS-ASAP, m/z calculated for  $C_{30}H_{34}N_2$  [M]<sup>+</sup> 423.2756, found 423.2787.

#### 3-(2,7-Di-tert-butyl-9,9-dimethylacridin-10(9H)-yl)benzonitrile (meta-2)



The title compound was obtained from **S1b** (0.78 g, 3.42 mmol) as colourless crystals (1.06 g, 2.51 mmol, 81%). M.P. 183 – 195 °C (DSC 198 °C). <sup>1</sup>H NMR (700 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  7.79 (dt, *J* = 7.8, 1.5 Hz, 1H, H<sub>4</sub>), 7.78 – 7.75 (m, 1H, H<sub>5</sub>), 7.63 – 7.62 (m, 1H, H<sub>3</sub>), 7.61 (dt, *J* = 7.5, 1.7 Hz, 1H, H<sub>6</sub>), 7.42 (d, *J* = 2.3 Hz, 2H, H<sub>14</sub>), 6.96 (dd, *J* = 8.6, 2.3 Hz, 2H, H<sub>10</sub>), 6.08 (d, *J* = 8.6 Hz, 2H, H<sub>9</sub>), 1.72 (s, 6H, H<sub>17</sub>), 1.35 (s, 18H, H<sub>13</sub>). <sup>13</sup>C NMR (176 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  144.0 (C<sub>11</sub>), 143.7 (C<sub>2</sub> or C<sub>1</sub>), 138.6 (C<sub>8</sub>), 136.5 (C<sub>6</sub>), 135.5 (C<sub>3</sub>), 132.2 (C<sub>5</sub>), 131.6 (C<sub>4</sub>), 130.4 (C<sub>15</sub>), 124.1 (C<sub>10</sub>), 122.9 (C<sub>14</sub>), 117.8 (C<sub>2</sub> or C<sub>1</sub>), 116.2 (C<sub>7</sub>), 114.4 (C<sub>9</sub>), 36.9 (C<sub>16</sub>), 34.6 (C<sub>12</sub>), 32.3 (C<sub>17</sub>), 32.2 (C<sub>13</sub>). Elemental analysis found: C, 85.29; H, 8.09; N, 6.62 %; molecular formula C<sub>30</sub>H<sub>34</sub>N<sub>2</sub> requires: C, 85.26; H, 8.11; N, 6.63 %. HRMS-ASAP, m/z calculated for C<sub>30</sub>H<sub>34</sub>N<sub>2</sub> [M]<sup>+</sup> 423.2756, found 423.2786.

### 4-(2,7-Di-tert-butyl-9,9-dimethylacridin-10(9H)-yl)benzonitrile (para-3)



The title compound was obtained from **S1c** (0.78 g, 3.42 mmol) as colourless crystals (0.98 g, 2.32 mmol, 75%). M.P. 286 – 288 °C (DSC 290 °C). <sup>1</sup>H NMR (700 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  7.84 – 7.81 (m, 2H, H<sub>3</sub>), 7.48 – 7.45 (m, 2H, H<sub>4</sub>), 7.44 (d, *J* = 2.3 Hz, 2H, H<sub>12</sub>), 7.02 (dd, *J* = 8.5, 2.3 Hz, 2H, H<sub>8</sub>), 6.35 (d, *J* = 8.5 Hz, 2H, H<sub>7</sub>), 1.68 (s, 6H, H<sub>15</sub>), 1.35 (s, 18H, H<sub>11</sub>). <sup>13</sup>C NMR (176 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  146.7 (C<sub>2</sub> or C<sub>1</sub>), 144.3 (C<sub>9</sub>), 137.9 (C<sub>6</sub>), 134.4 (C<sub>3</sub>), 132.2 (C<sub>13</sub>), 128.9 (C<sub>4</sub>), 123.4 (C<sub>8</sub>), 122.2 (C<sub>12</sub>), 118.0 (C<sub>2</sub> or C<sub>1</sub>), 115.8 (C<sub>7</sub>), 110.3 (C<sub>5</sub>), 36.7 (C<sub>14</sub>), 34.2 (C<sub>10</sub>), 31.6 (C<sub>11</sub>), 30.9 (C<sub>15</sub>). Elemental analysis found: C, 85.31; H, 8.12; N, 6.57 %; molecular formula C<sub>30</sub>H<sub>34</sub>N<sub>2</sub> requires: C, 85.26; H, 8.11; N, 6.63 %. HRMS-ASAP, m/z calculated for C<sub>30</sub>H<sub>34</sub>N<sub>2</sub>[M]<sup>+</sup> 423.2756, found 423.2800.



### S3. <sup>1</sup>H and <sup>13</sup>C Spectroscopic Characterisation of Synthesised Compounds

Figure S3.1. <sup>1</sup>H NMR of *ortho-1*.



Figure S3.2. <sup>13</sup>C NMR of *ortho-1*.



Figure S3.3. <sup>1</sup>H NMR of *meta-2*.



Figure S3.4. <sup>13</sup>C NMR of *meta-2*.



Figure S3.5. <sup>1</sup>H NMR of *para-3* 



Figure S3.4. <sup>13</sup>C NMR of *para-3*.

### **S4. Variable-Temperature NMR**

We performed VT NMR measurements on *ortho-1*, *meta-2*, *para-3* to determine if we could measure the energy barriers to exchange of the methyl group environments due to rotation around the hindered C–N bond connecting the acridine to the benzonitrile fragment. Only the *ortho-1* isomer showed an exchange process that reached slow exchange regime in the accessible temperature range (from room temperature down to –98 °C). VT <sup>1</sup>H NMR spectra were acquired to facilitate analysis using a two-spin system model in the WinDNMR<sup>19</sup> software package. In order to obtain a solution of *ortho-1* with a low freezing point (5.7 mg in 0.8 mL) for <sup>1</sup>H NMR analysis, a mixture of CS<sub>2</sub> (0.6 mL) with CD<sub>2</sub>Cl<sub>2</sub> (0.2 mL) was used as solvent. A series of spectra ranging from 24 °C to –98 °C were recorded (Figure S4.1).



**Figure S4.1.** Partial <sup>1</sup>H VT NMR spectra of *ortho-1*. Peaks corresponding to the methyl group environments X/X' are observed as averaged signals in the fast exchange regime, but appear as individual distinct signals at low temperature in the slow exchange regime.

Analysis of the <sup>1</sup>H NMR spectra reveals that, within the temperature range studied, signals corresponding to the methyl groups broaden, merge into the baseline, and then re-emerge as two separate peaks as the temperature is decreased. We selected six spectra for further analysis, choosing temperatures close to the transition from the fast to the slow exchange regimes (Figure S4.2). Lineshape analysis was performed to derive rate constants by comparison to model spectra produced using WinDNMR.



**Figure S4.2.** <sup>1</sup>H VT NMR spectra of *ortho-1* used for lineshape analysis. The dashed blue lines illustrate the resolution of single peaks into pairs of peaks as temperature decreases.

Activation energy barriers for the rotation of the methyl groups were calculated (Table S4.1) for each of the five temperatures using equation S4.1:

$$\Delta G^{\dagger} = -RT \ln \frac{k_r h}{k_B T}$$

**Equation S4.1.** A variation of the Eyring equation, where  $k_r$  is the measured rate constant,  $k_B$  is the Boltzmann constant, *T* is temperature, *h* is Planck's constant, and *R* is the ideal gas constant.

Entry	<b>Temperature / K</b>	$\Delta \mathbf{G}^{\dagger}$ / kJ mol <sup>-1</sup>
1	265.6	45.0
2	260.4	45.4
3	255.0	45.5
4	244.4	46.3
5	239.1	46.8
6	228.5	47.4

**Table S4.1.** Calculated activation energies ( $\Delta G^{\dagger}$ ) for the rotation of the methyl groups.

A line was fitted (Figure S4.3) to a plot of  $\Delta G^{\ddagger}$  vs *T*. The slope of the line corresponds to  $-\Delta S^{\ddagger}$  and the y-axis intercept to  $\Delta H^{\ddagger}$ . The entropy of activation  $\Delta S^{\ddagger}$  was calculated to be 66.2 J mol<sup>-1</sup> K<sup>-1</sup> and enthalpy of activation  $\Delta H^{\ddagger}$  was calculated to be 62.5 kJ mol<sup>-1</sup>.



**Figure S4.3.** A plot of the experimentally measured free energy of activation  $\Delta G^{\dagger}$  for rotation of *ortho*-1 as a function of temperature.

As we did not observe slow exchange for *meta*-2 and *para*-3 down to temperatures as low as -98 °C, we can estimate that  $\Delta G^{\dagger}$  of the ring rotation must be <33 kJ mol<sup>-1</sup>, making the assumption that the limiting chemical shifts of the methyl groups would be similar to those observed for *ortho*-1.

### **S5. X-ray Crystallographic Analysis**

Identification code	ortho-1	meta-2	para-3
Empirical formula	$C_{30}H_{34}N_2$	$C_{30}H_{34}N_2$	$C_{30}H_{34}N_2$
Formula weight	422.59	422.59	422.59
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/Å	15.4617(13)	18.260(10)	10.5606(10)
b/Å	13.9720(8)	5.891(3)	13.2594(12)
c/Å	11.5956(15)	23.197(12)	17.6725(16)
β/°	100.466(8)	94.999(12)	98.270(4)
Volume/Å <sup>3</sup>	2463.3(4)	2486(2)	2448.9(4)
Z	4	4	4
$\rho_{calc}g/cm^3$	1.139	1.129	1.146
μ/mm <sup>-1</sup>	0.066	0.065	0.066
F(000)	912.0	912.0	912.0
<b>Reflections collected</b>	22729	16428	50071
Independent refl., R <sub>int</sub>	5379, 0.2040	4572, 0.2134	6501, 0.0512
Data/restraints/parameters	5379/0/297	4572/0/298	6501/0/297
Goodness-of-fit on F <sup>2</sup>	0.955	0.903	1.023
Final R₁ [I≥2σ (I)]	0.0793	0.0854	0.0470
Final wR <sub>2</sub> [all data]	0.1791	0.1961	0.1240
Largest diff. peak/hole / e Å <sup>-3</sup>	0.24/-0.23	0.38/-0.33	0.34/-0.30

**Table S5.1**. X-ray crystallographic data and structure refinement parameters.

### ortho-1

Crystals of *ortho-1* suitable for X-ray diffraction (Figure S5.1) were grown by slow evaporation of a  $CS_2$  and  $CD_2Cl_2$  (0.6 mL:0.2 mL) solution.



**Figure S5.1.** X-ray crystal structure of *ortho*-1 viewed from (a) above and (b) in the plane of the acridine ring system.

Crystal System: Monoclinic Space group: P2<sub>1</sub>/c Unit Cell Parameters: a = 15.4617(13) Å, b = 13.9720(8) Å, c = 11.5956(15) Å,  $\alpha$  = 90 °,  $\beta$  = 100.466(8) °,  $\gamma$  = 90 °, V = 2463.3(4) Å<sup>3</sup>, Z = 4.

### meta-2

Crystals of *meta-2* suitable for X-ray diffraction (Figure S5.2) were grown by layer diffusion of a saturated dichloromethane and isopropanol (1:4) solution.



**Figure S5.2.** X-ray crystal structure of *meta-2* viewed from (a) above and (b) in the plane of the acridine ring system.

Crystal System: Monoclinic Space group: P2<sub>1</sub>/c Unit Cell Parameters: a = 18.260(10) Å, b = 5.891(3) Å, c = 23.197(12) Å,  $\alpha = 90$  °,  $\beta = 94.999(12)$  °,  $\gamma = 90$  °, V = 2486(2) Å<sup>3</sup>, Z = 4. para-3

Crystals of *para-3* suitable for X-ray diffraction (Figure S5.3) were grown by slow evaporation of a  $CS_2$  and  $CD_2Cl_2$  (0.6 mL:0.2 mL) solution.



**Figure S5.3.** X-ray crystal structure of *para-3* viewed from (a) above and (b) in the plane of the acridine ring system.

Crystal System: Monoclinic Space group: P2<sub>1</sub>/c Unit Cell Parameters: a = 10.5606(10) Å, b = 13.9720(8) Å, c = 17.6725(16) Å,  $\alpha$  = 90 °,  $\beta$  = 98.270(4) °,  $\gamma$  = 90 °, V = 2448.9(4) Å<sup>3</sup>, Z = 4.

### **S6.** Analysis of Crystal Packing

In order to discern if the differences in the planarity of the acridine ring systems shown in Figures S5.1–S3.3 arise because of specific crystal packing phenomena, we performed calculations to model the Hirshfeld surfaces of *ortho-1*, *meta-2*, and *para-3* and to estimate the interaction energies between molecules in the crystals.

Hirshfeld surfaces<sup>20</sup> give insights into the interactions between molecules in the crystal lattices. We calculated Hirshfeld surfaces for the crystal packing structures in CrystalExplorer17<sup>20</sup> using an isovalue of 0.5 and mapping the normalised contact distance,  $d_{norm}$ . The surfaces highlight (Figures S6.1, S6.3 and S6.5) in red any regions in which the molecular surfaces meet at distances shorter than the sum of van der Waals radii, while white and blue illustrate regions where they meet at distances that are the sum of the van der Waals radii or longer, respectively. Overall, the Hirshfeld surfaces reveal there are only a few contacts that are slightly shorter than the sum of van der Waals radii – there are only a small number of red patches, which are faint in colour and small in size. This data suggests that there are no strong and specific noncovalent interactions in the solid state that direct the crystal packing. The most significant close contact found was an intermolecular C=N···H–C interaction present in the lattice of *para-3*.

We performed DFT calculations to quantify the interaction energies between neighbouring molecules in the solid state using the CE-B3LYP [B3LYP/6-31G(d,p)] energy model in CrystalExplorer17.20 Based on the X-ray crystal structure coordinates, a cluster was generated around a central molecule, extending to molecules that come within 3.8 Å of the central molecule at any point. As each of the crystal structures of ortho-1, meta-2, and para-3 have only one unique molecule in each of the unit cells (Z' = 1), all of the surrounding molecules are related to the central molecule by a symmetry operation (labelled 'Symmetry Op.' in Tables S6.1, S6.2 and S6.3). These energy calculations allow us to elucidate the total interaction energies (Etot, in kJ·mol-1) between neighbouring molecules, based on the individual components for electrostatic ( $E_{ele}$ ), polarization ( $E_{pol}$ ), dispersion ( $E_{dis}$ ), and repulsion  $(E_{rep})$  energies. In each of the Tables below, N indicates the number of molecules of a particular symmetry operation included in the cluster. R is the distance between the molecular centroids (mean atomic position) of the central molecule and the molecule generated by the given symmetry operation. A colour code is given for each table entry, which matches the colouring of the relevant molecules in the corresponding cluster diagrams, Figures S6.2, S6.4 and S6.6.



**Figure S6.1**. A Hirshfeld surface analysis of *ortho-1*, viewed along the crystallographic (b) *a*-axis, (c) *b*-axis, and (d) *c*-axis, shows a lack of significant close contacts.

**Table S6.1**. Calculated intermolecular interaction energies (in  $kJ \cdot mol^{-1}$ ) for the solid-state structure of *ortho*-1.

N	Symmetry Op.	<i>R</i> / Å	Eele	E <sub>pol</sub>	Edis	Erep	E <sub>tot</sub>
1	-x, -y, -z	15.54	-0.1	-0.6	-1.9	0.0	-2.2
1	-x, y+1/2, -z+1/2	11.09	-2.1	-4.9	-17.8	9.1	-15.7
0	-x, -y, -z	9.81	-1.6	-0.1	-18.9	6.5	-14.2
1	x, -y+1/2, z+1/2	6.77	-22.2	-0.0	-98.4	64.8	-69.2
0	-x, -y, -z	11.99	-1.6	-4.1	-17.5	6.4	-16.0
0	-x, y+1/2, -z+1/2	9.81	-16.0	-4.1	-37.0	24.9	-36.8
0	x, y, z	11.60	-0.2	0.0	-7.7	0.8	-6.4
0	x, -y+1/2, z+1/2	11.97	-0.7	-0.1	-14.2	7.0	-8.8
0	-x, -y, -z	10.10	-5.6	-0.0	-38.3	17.9	-28.2
0	-x, -y, -z	9.18	9.0	-5.0	-11.4	6.9	0.2



**Figure S6.2**. The cluster of molecules used to model intermolecular interaction energies in Table S6.1. The central molecule is coloured according to atom type (C, grey; H, white; N, blue) and surrounding molecules are coloured to match the colour code in Table S6.1.



**Figure S6.3.** A Hirshfeld surface analysis of *meta-2*, viewed along the crystallographic (b) *a*-axis, (c) *b*-axis, and (d) *c*-axis, shows a lack of significant close contacts.

N	Symmetry Op.	<i>R</i> / Å	Eele	$E_{\rm pol}$	Edis	Erep	E <sub>tot</sub>
2	-x, y+1/2, -z+1/2	10.45	-3.5	-0.1	-26.6	13.1	-18.8
0	-x, -y, -z	15.34	-3.1	-0.0	-14.6	12.3	-8.4
2	x, y, z	5.89	-15.9	-1.2	-89.8	51.1	-64.3
1	-x, y+1/2, -z+1/2	13.36	-0.8	-0.5	-6.4	4.4	-4.0
1	-x, -y, -z	13.75	-0.0	-0.1	-4.9	0.5	-4.0
1	x, -y+1/2, z+1/2	12.24	-7.8	-5.9	-11.9	10.7	-16.4
1	x, -y+1/2, z+1/2	11.77	-0.3	-0.2	-9.8	3.7	-6.7
0	-x, y+1/2, -z+1/2	9.58	-6.9	-0.2	-40.5	21.1	-29.6
0	-x, -y, -z	11.62	-2.6	-1.6	-25.4	13.2	-17.9
0	-x, -y, -z	12.58	-0.5	-5.0	-12.4	2.5	-13.5

**Table S6.2**. Calculated intermolecular interaction energies (in  $kJ \cdot mol^{-1}$ ) for the solid-state structure of *meta*-2.



**Figure S6.4**. The cluster of molecules used to model intermolecular interaction energies in Table S6.2. The central molecule is coloured according to atom type (C, grey; H, white; N, blue) and surrounding molecules are coloured to match the colour code in Table S6.2.



**Figure S6.5**. A Hirshfeld surface analysis of *para-3*, viewed along the crystallographic (b) *a*-axis, (c) *b*-axis, and (d) *c*-axis, shows a lack of significant close contacts.

**Table S6.3**. Calculated intermolecular interaction energies (in kJ·mol<sup>-1</sup>) for the solid-state structure of *para*-3.

N	Symmetry Op.	<i>R</i> / Å	Eele	$E_{\rm pol}$	Edis	Erep	Etot
2	-x, y+1/2, -z+1/2	11.13	-3.1	-0.1	-36.9	19.4	-23.5
1	-x, -y, -z	6.45	-17.2	-3.2	-64.2	34.7	-55.0
1	x, -y+1/2, z+1/2	13.00	-2.5	-4.7	-15.3	10.4	-13.0
1	x, -y+1/2, z+1/2	9.19	-8.1	-0.2	-54.8	34.2	-35.2
0	-x, -y, -z	10.41	-0.6	-4.4	-15.1	2.9	-15.2
1	x, y, z	13.26	-12.9	-1.2	-14.4	21.6	-13.7
1	-x, -y, -z	7.00	-11.8	-1.4	-52.1	22.7	-44.8
0	-x, y+1/2, -z+1/2	12.25	-2.8	-0.1	-26.2	13.1	-17.7
0	-x, -y, -z	10.76	-2.5	-0.0	-19.4	10.4	-13.1



**Figure S6.6**. The cluster of molecules used to model intermolecular interaction energies in Table S6.3. The central molecule is coloured according to atom type (C, grey; H, white; N, blue) and surrounding molecules are coloured to match the colour code in Table S6.3.

### **S7. Thermal and Electrochemical Data**



Figure S7.1. TGA curves of acridine-benzonitrile hybrid compounds.



Figure S7.2. DSC curves of ortho-1.



Figure S7.3. DSC curves of *meta-2*.



Figure S7.4. DSC curves of *para-3*.



Figure S7.5. Cyclic voltammetry scans of dilute 1  $\mu$ g/ml dichloromethane solutions of acridine-benzonitrile derivatives.

 Table S7.1. Thermal and electrochemical characteristics of acridine-benzonitrile derivatives.

Compound	T <sub>g</sub> , ⁰Cª	T <sub>M</sub> , °C <sup>a</sup>	T <sub>cr</sub> , °C <sup>a</sup>	T <sub>sub</sub> *, °C <sup>b</sup>	IP <sup>CV</sup> , eV <sup>c</sup>	EA <sup>CV</sup> , eV°
ortho-1	97	242	115	241	5.39	2.30
meta-2	-	198	151	252	5.34	2.30
para-3	-	290	265	252	5.30	2.31

<sup>a</sup>Determined by DSC; <sup>b</sup>Determined by TGA. \*Compounds sublimed during the TGA experiment; <sup>c</sup>Ionization potentials and electron affinities were determined by CV in  $CH_2Cl_2$  solutions.

**S8. Ground- and excited-state DFT calculations** 



**Figure S8.1.** Ground state (rBMK/6-31G(d)) and first excited state (TD-DFT BMK/6-31G(d)) optimized structures of *ortho-1*, *meta-2* and *para-3* along with the D-A bond length and dihedral angle values.



**Figure S8.2.** Theoretical UV/Vis absorption spectra of (a) *ortho*-1, (b) *meta*-2 and (c) *para*-3 along with corresponding oscillator strengths (TDA-DFT rBMK-6-31G(d)).

### **S9.** Steady-State Absorbance and Emission Spectra

### a) ortho-1

#### b) *meta-2*



Figure S9.1. Absorbance spectra of 20  $\mu$ M a) *ortho*-1 b) *meta*-2 and c) *para*-3 in cyclohexane (black), chloroform (red) and dichloromethane (blue).

a) ortho-1

b) *meta-2* 



**Figure S9.2.** Emission spectra ( $\lambda_{ex}$ =320 nm, 293 K) of 20  $\mu$ M a) *ortho*-1 b) *meta*-2 and c) *para*-3 in cyclohexane (black), toluene (red), chloroform (blue) and dichloromethane (pink) d) normalised emission of 1% w/w *ortho*-1 (black), *meta*-2 (red), *para*-3 (blue) in zeonex ( $\lambda_{ex}$ =300 nm, 293 K).

### S10. Aerated vs Degassed Spectra in Toluene



**Figure S10.** Aerated (black) and degassed (black) spectra of 20  $\mu$ M a) *ortho-1* b) *meta-2* and c) *para-3* in toluene ( $\lambda_{ex}$ =300 nm, 293 K).



S11. Intensity vs Delay Time of Isomers at Different Temperatures

**Figure S11.** Intensity vs delay time of 10% DPEPO (left) and 1% Zeonex (right) films of w/w a) *ortho*-1 b) *meta*-2 and c) *para*-3 80 K (black), 120 K (red), 160 K (green), 200 K (blue), 240 K (cyan), 280 K (pink) and 300 K (grey).

## **S12.** Laser Pulse Fluence vs Integrated Delayed Emission for Isomers in Zeonex and DPEPO Matrices



**Figure S12.** Integrated delayed emission against laser pulse fluence ( $\mu$ J) ( $\lambda_{ex}$ =337 nm, 293 K) of a) *ortho*-1 in zeonex, b) *ortho*-1 in DPEPO c) *meta*-2 in zeonex d) *meta*-2 in DPEPO e) *para*-3 in zeonex and f) *para*-3 in DPEPO. \*TD=time delay after laser pulse.

S13. Normalised Spectra of Isomers in DPEPO Matrix in the Prompt Time Region



**Figure S13.** Emission spectra of 10% w/w a) *ortho-1* b) *meta-2* and c) *para-3* in DPEPO ( $\lambda_{ex}$ =337 nm, 300 K), showing the prompt, short timescale region

**S14. Spectra of Isomers in DPEPO Matrix at Varying Delay Times and Temperatures** a)



**Figure S14.** Emission spectra of 10% w/w a) *ortho-1* b) *meta-2* and c) *para-3* in DPEPO at varying temperatures ( $\lambda_{ex}$ =337 nm).

### S15. Exponential and Kinetic Emission Decay Fits in Zeonex at 300 K



Figure S15.1 Exponential fitting of *ortho*-1 emission decay.



Figure S15.2 Kinetic fitting of ortho-1 emission decay.



Figure S15.3 Exponential fitting of *meta-2* emission decay.



Figure S15.4 Kinetic fitting of *meta-2* emission decay.

![](_page_36_Figure_0.jpeg)

Figure S15.5 Exponential fitting of *para*-3 emission decay.

![](_page_36_Figure_2.jpeg)

Figure S15.4 Kinetic fitting of para-3 emission decay.

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