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Electronic Supplementary Information

for

Correlating Structural Changes with the Photophysics of

Terrylenediimide Films during Spontaneous Annealing

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Synthesis



Synthesis of Broken C₂₃TDI

A mixture of **NMI-Br** (466 mg, 0.78 mmol), **S2** (**PMI-Bpin**) (300 mg, 0.39 mmol), Aliquat 336 (2 drops), ethanol (1 mL), and toluene (10 mL) was degassed and to was combined with $Pd_2(dba)_3$ (28 mg, 31 µmol),Tri-tert-butyl phosphonium tetrafluoroborate (18 mg, 62 µmol) and a solution of K₃PO₄ (402 mg, 1.95 mmol) in 1 mL deoxygenated water. The mixture was heated at 90 °C for 48 h with vigorous stirring. After cooling down to room temperature, the resulting mixture was extracted with dichloromethane (100 mL) twice, and the organic layer was dried over NaSO₄. The organic solvent was concentrated in reduced pressure to yield a red solid. The pure **Broken** C₂₃**TDI** (360 mg, 80 %) was obtained by silica gel column chromatography (1:2 dichloromethane/hexane).

¹H NMR (500 MHz, Chloroform-*d*) δ 8.80 – 8.62 (m, 4H), 8.59 (d, *J* = 7.8 Hz, 1H), 8.53 (d, *J* = 8.2 Hz, 1H), 8.52 – 8.46 (m, 2H), 7.84 (m, 2H), 7.65 (d, *J* = 7.7 Hz, 1H), 7.62 (t, *J* = 7.9 Hz, 1H), 7.49 (t, *J* = 7.9 Hz, 1H), 7.42 (d, *J* = 8.3 Hz, 1H), 5.21 (m, 2H), 2.27 (pd, *J* = 11.4, 9.5, 6.3 Hz, 4H), 1.93 – 1.78 (m, 4H), 1.72 (dq, *J* = 11.8, 6.6 Hz, 1H), 1.61 (dd, *J* = 12.1, 3.4 Hz, 1H), 1.40 – 1.14 (m, 70H), 0.86 (dt, *J* = 11.2, 7.2 Hz, 12H).



Broken $C_{23}TDI$ (1.9 g, 1.6 mmol) was dissolved in diglyme (15 ml), and mixed with ethanolamine (50 ml) and K₂CO₃ (10 g, 72 mmol). The mixture was purged with nitrogen and stirred at 150 for 6 hours. After cooling, the reaction mixture was poured over water and filtered, and the remaining solids were purified through flash chromatography (5:1 Dichloromethane: Hexanes \rightarrow Dichloromethane) to produce pure C₂₃TDI (1.2 g, 65%). ¹H NMR (500 MHz, Chloroform-*d*) δ 8.70 – 8.57 (m, 8H), 8.53 (d, *J* = 8.0 Hz, 4H), 5.25 – 5.13 (m, 2H), 2.34 – 2.18 (m, 4H), 1.86 (m, 4H), 1.39 – 1.26 (m, 8H), 1.25 – 1.11 (m, 64H), 0.82 (t, *J* = 7.0 Hz, 12H).



Figure S1: Absorption (solid line) and emission data (dashed line) for fresh (black) and aged (red) film samples. Emission scaled to the OD at $\lambda_{ex} = 585$ nm for the respective sample.

	542 nm	623 nm	680 nm	Avg	St. Dev
А	0.051	0.067	0.063		
α	0.05113	0.044	0.036		
p	0.38	0.36	0.34	0.36	0.018
t_1 (hrs)	12.06	12.10	12.52	12.22	0.21
t_2 (hrs)	19.90	19.80	19.64	19.78	0.11
τ_1 (hrs)	-2.58	2.73	2.47	2.59	0.11
τ_2 (hrs)	-1.54	1.55	1.49	1.52	0.03

Table S1: Values from fitting of time-resolved UV-Vis, Figure 2 in the main text.



Figure S2: A) Steady-state absorption spectra of C_{23} TDI film at 60 °C with initial OD 0.07 at $\lambda_{max} = 621$ nm collected in 5 minutes increments. Isosbestic points are circled. B) kinetic traces of representative wavelengths (squares), with fits (solid lines).



Figure S3: Steady-state absorption spectra of C_{23} TDI films at stored at 4 °C (a) and -22 °C (b), taken at various delay times following film preparation.



Figure S4: A) Steady-state absorption spectra of C_{23} TDI film with initial OD 0.157 at $\lambda_{max} = 621$ nm collected in 30 minutes increments. Isosbestic points are circled. B) kinetic traces of representative wavelengths (open squares), with fits (solid lines).

	542 nm	623 nm	680 nm	Avg	St. Dev
А	0.061	0.088	0.082		
α	0.077	0.065	0.053		
p	0.42	0.43	0.48	0.45	0.027
t_1 (hrs)	29.21	29.41	29.90	29.51	0.29
t_2 (hrs)	35.20	35.09	35.18	35.16	0.05
τ_1 (hrs)	-3.66	3.54	3.07	3.42	0.25
τ_2 (hrs)	-1.74	1.73	1.57	1.68	0.078

Table S2: Values from fitting of time-resolved UV-Vis, Figure S4.



Figure S5: Steady-state absorption spectra of C_{23} TDI films at 0, 18, and 36 hours after film preparation. (A) Films prepared on a butylated substrate. (B) Films prepared under identical conditions, one film stored open to air (solid line) and the other stored under vacuum (dashed line).

X-ray Scattering Analysis





Figure S6: 2D GIWAXS scattering plot of C_{23} TDI film 1 on glass at 5 (a) and 15 (b) hours after preparation, film 2 on glass at 18 (c) and 21 (d) hours after preparation, film 3 on a butyl surface at 22 (e) and 32 (f) hours after preparation, and film 4 on glass 1 week after preparation (g).

	a (Å)	b (Å)	c (Å)	α (°)	β (°)	y (?)	V (Å ³)
GIWAXS	5.90	9.22	37.37	89.34	92.26	86.35	2026.9
PXRD	5.44	37.93	9.03	87.7	87.66	87.8	1816

Table S3: Unit cell parameters extracted from GIWAXS and PXRD data sets.



Figure S6: Image of two $C_{23}TDI$ molecules according to the packing derived from GIWAXS analysis, viewed along π - π stacking plane. Slipping distances are marked. Aliphatic tails have been removed for clarity.



Figure S7: Proposed packing arrangement of the initial metastable state of $C_{23}TDI$ films.

Time-Resolved Optical Spectroscopy

Prior to kinetic analysis, the fsTA data are background/scatter-subtracted and chirp-corrected, and the visible and NIR data sets are spectrally merged (Surface Xplorer 4, Ultrafast Systems, LLC). The kinetic analysis was performed using home written programs in MATLAB¹ and was based on a global fit to selected single-wavelength kinetics. The time-resolution is given as w = 300 fs (full width at half maximum, FWHM); the assumption of a uniform instrument response across the frequency domain and a fixed time-zero (t_0) are implicit in global analysis. The kinetic data from multiple different wavelengths are fit using the global analysis described below. Each wavelength is given an initial amplitude that is representative of the spectral intensity at time t_0 , and varied independently to fit the data. The time/rate constants and t_0 are shared between the various kinetic data and are varied globally across the kinetic data in order to fit the model(s) described below. We globally fit the dataset to a specified kinetic model and use the resultant populations to deconvolute the dataset and reconstruct species-associated spectra. We use a first-order kinetic model with rate matrix *K*:

$$\underline{K} = \begin{pmatrix} -k1 & 0 & 0\\ k1 & -k2 & 0\\ 0 & k2 & k3 \end{pmatrix}$$
(S1)

The MATLAB program numerically the solves the differential equations through matrix methods,² then convolutes the solutions with a Gaussian instrument response function with width w (FWHM), before employing a least-squares fitting using a Levenberg-Marquardt or Simplex method to find the parameters which result in matches to the kinetic data.

Once the fit parameters are established, they are fed directly into the differential equations, which were solved for the populations of the states in model—i.e., A(t), B(t), and C(t). Finally, the

raw data matrix (with all the raw data) is deconvoluted with the populations as functions of time to produce the spectra associated with each species.



Figure S9: fsTA analysis of fresh C_{23} TDI film. a) Kinetic data and overlaid fit at selected wavelengths, b) model population c) species-associated spectra.



Figure S10: fsTA analysis of aged C_{23} TDI film. a) Kinetic data and overlaid fit at selected wavelengths, b) model population c) species-associated spectra.



Figure S11: fsTA analysis of aged C_{23} TDI film at various times following excitation at 540 nm.



Figure S12: fsTA analysis of aged C_{23} TDI film, excited at 540 nm. a) Kinetic data and overlaid fit at selected wavelengths, b) model population c) species-associated spectra.

References

- 1. The MathWorks, I., Natick, Massachusetts, United States.
- 2. Berberan-Santos, M. N.; Martinho, J. M. G., The integration of kinetic rate equations by

matrix methods. J. Chem. Ed. 1990, 67, 375.