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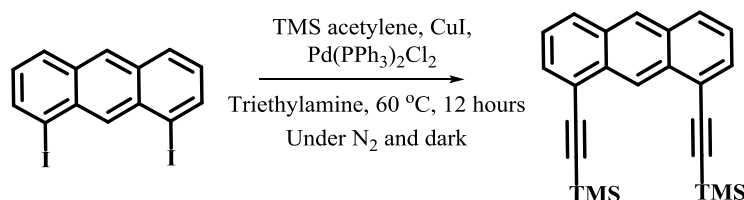
Supporting information for article:

**A new tecton with parallel halogen-bond donors: A path to
supramolecular rectangles**

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Aakeröy**

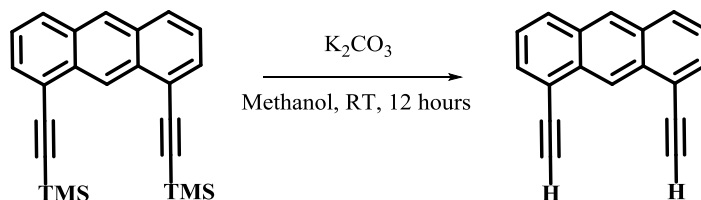
S1. Synthesis of the halogen bond donor

S1.1. Synthesis of 1,8-bis((trimethylsilyl)ethynyl)anthracene



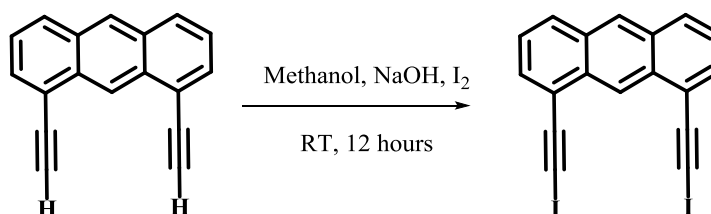
1,8-Diiodoanthracene (1.00 g, 2.33 mmol), trimethylsilylacetylene (0.72 ml, 5.12 mmol), CuI (0.044 g, 0.23 mmol), and bis(triphenylphosphine)palladium(II) dichloride (0.098 g, 0.14 mmol) were dissolved in 50 ml of degassed trimethylamine. The mixture was stirred overnight at room temperature under a dinitrogen atmosphere under dark. Completion of reaction was confirmed with TLC. The reaction mixture was concentrated in vacuo and the residue was dissolved in diethyl ether (50 ml). Ethereal solution was washed with 1M HCl (10 ml), water (2 X 20 ml) and saturated NaCl solution (20 ml). The organic layer was dried with anhydrous MgSO₄ and concentrated in Vacuo. The crude product was purified by flash chromatography in 50:1 hexane: ethyl acetate yielding the final product as a yellow powder. Yield - (0.72 g, 83%); ¹H NMR (δH; 400 MHz, CDCl₃): 0.39 (s, 18H), 7.43 (t, 2H), 7.98 (d, 2H), 8.00 (t, 2H), 8.43 (s, 1H), 9.33 (s, 1H).

S1.2. Synthesis of 1,8-diethynylantracene



1,8-Bis((trimethylsilyl)ethynyl)anthracene (0.70 g, 1.89 mmol) and potassium carbonate (0.78 g, 5.66 mmol) were stirred in methanol (50 mL) at room temperature for 12 hours. The solution was then diluted with ethyl ether (50 mL) and washed with water (4 x 50 mL). The solvent was removed on a rotary evaporator and the residue was obtained as a yellow powder. Yield - (0.30 g, 71 %). ¹H NMR (δH; 400 MHz, CDCl₃): 3.62 (s, 2H), 7.48 (t, 2H), 7.79 (d, 2H), 8.03 (t, 2H), 8.47 (s, 1H), 9.44 (s, 1H).

S1.3. Synthesis of 1,8-bis(iodoethynyl)anthracene



To a solution of 1,8-diethynylanthracene (0.30 g, 1.33 mmol) in methanol (30 mL), were added, simultaneously and dropwise over 30 min, an almost saturated solution of iodine (0.74 g, 2.91 mmol) in methanol and a 10 % water solution of sodium hydroxide (0.21 g, 5.32 mmol), while the mixture was maintained under vigorous stirring. The mixture was stirred for 12 hours and then water was added until a precipitate formed, which was filtered and washed first with water (20 mL), then with a saturated solution of sodium bisulfite (10 mL), then with water (20 mL) again. The solid was dried and collected the final product as a yellow powder. Yield - (0.48 g, 76 %). ¹H NMR (δH; 400 MHz, CDCl₃): 7.45 (t, 2H), 7.72 (d, 2H), 8.01 (t, 2H), 8.44 (s, 1H), 9.32 (s, 1H).

S2. Characterization - NMR spectra

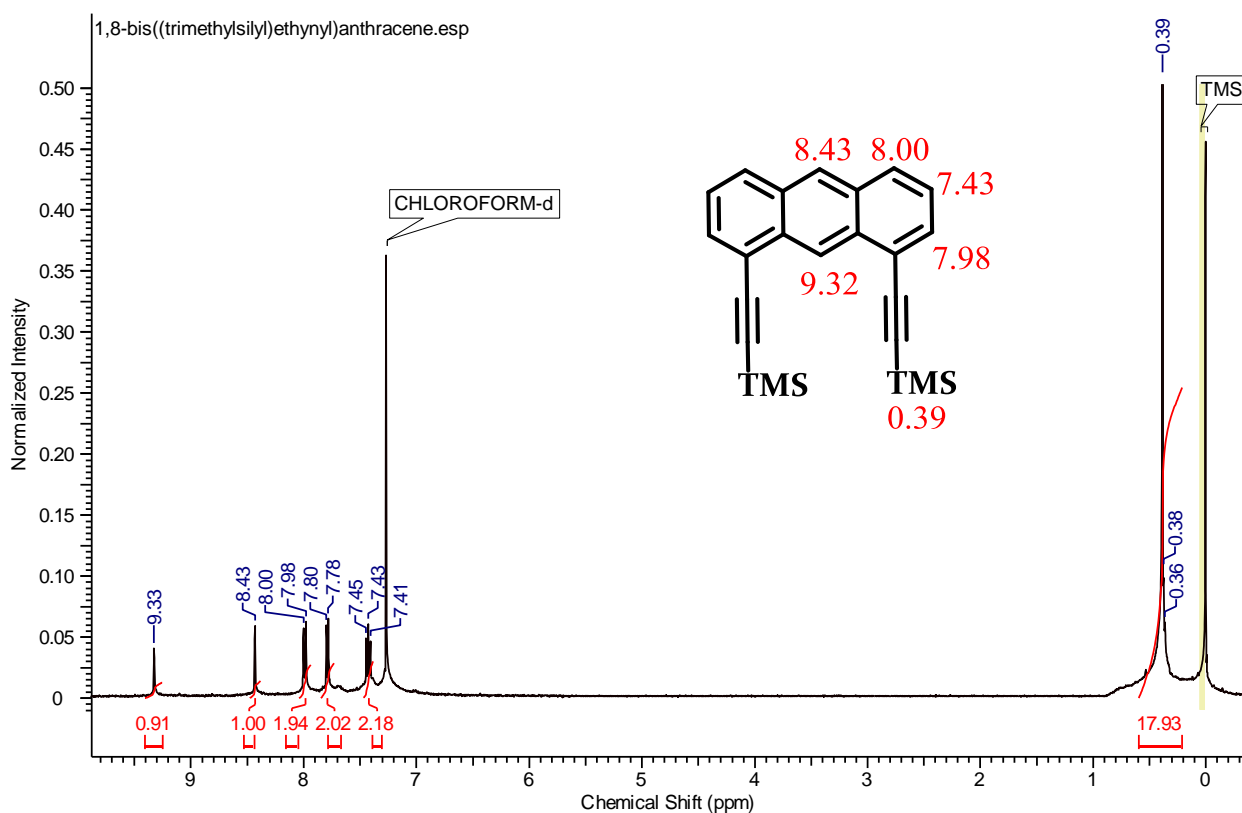
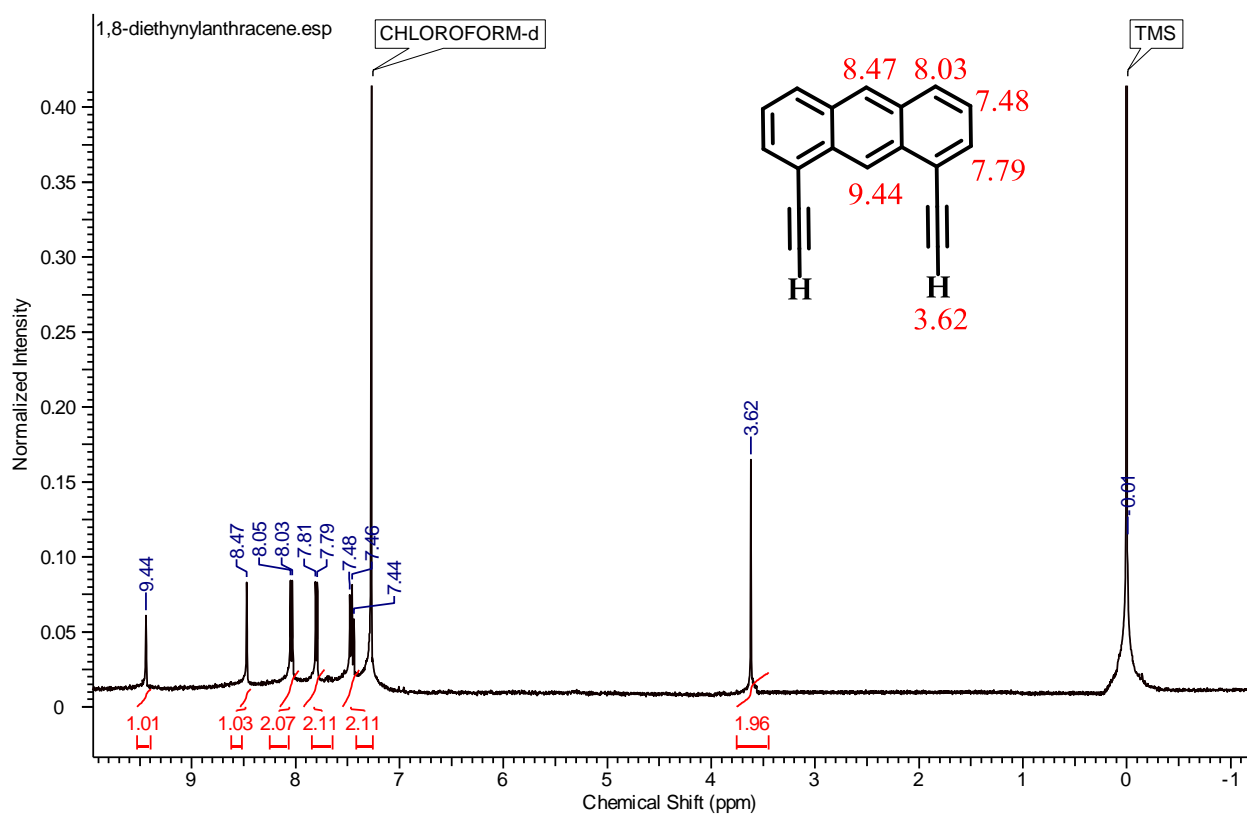
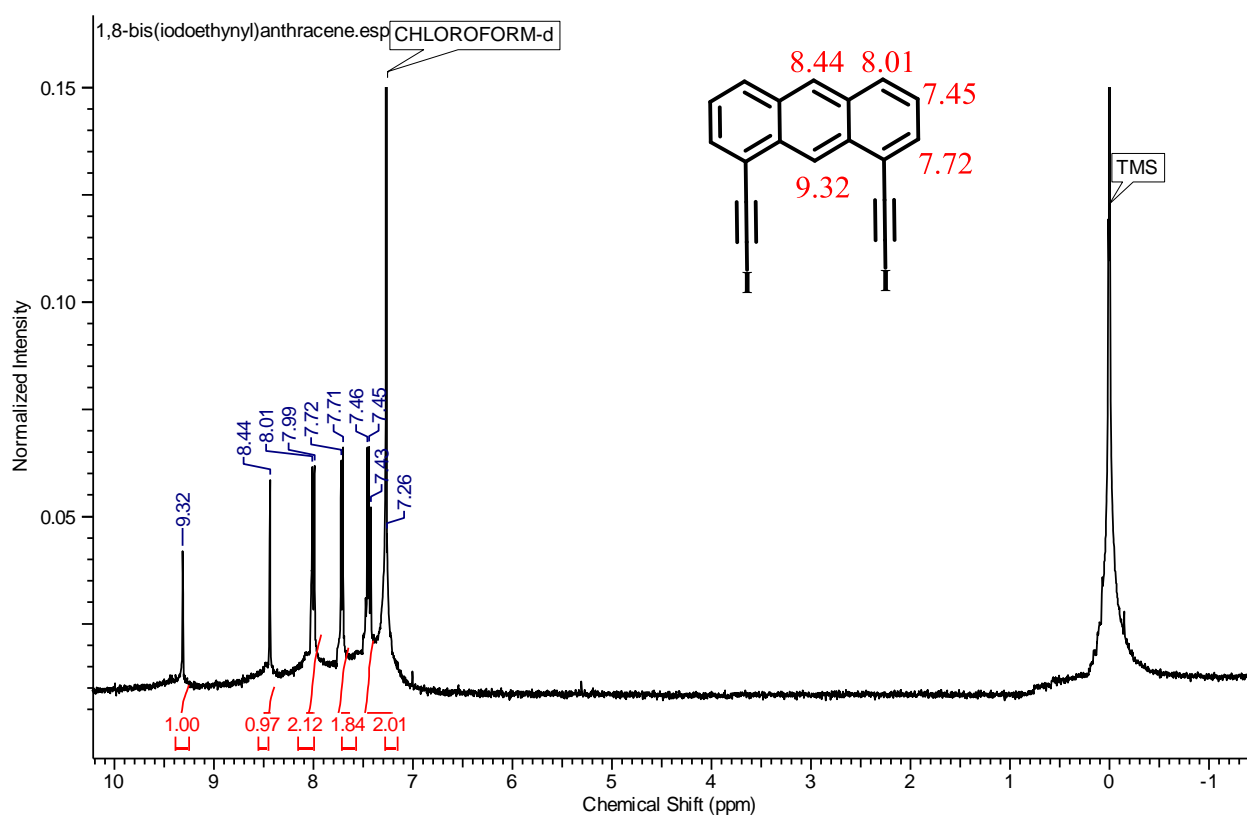


Figure S1 ¹H NMR of 1,8-bis((trimethylsilyl)ethynyl)anthracene

**Figure S2** ^1H NMR of 1,8-diethynylantracene**Figure S3** ^1H NMR of 1,8-diethynylantracene

S3. Crystallographic data

Datasets for **DIEA:BipyNO**, **DIEA:Bpe** and **DIEA:Bpen** were collected on a Bruker APEX II system with MoK α radiation using APEX2 software.¹ Initial cell constants were found by small widely separated “matrix” runs. Data collection strategies were determined using COSMO.² Scan speed and scan widths were chosen based on scattering power and peak rocking curves. All datasets were collected at -153 °C using an Oxford Cryostream low-temperature device.

Unit cell constants and orientation matrix were improved by least-squares refinement of reflections thresholded from the entire dataset. Integration was performed with SAINT,³ using this improved unit cell as a starting point. Precise unit cell constants were calculated in SAINT from the final merged dataset. Lorenz and polarization corrections were applied. Multi-scan absorption corrections were performed with SADABS.⁴

Data were reduced with SHELXTL.⁵ The structures were solved in all cases by direct methods without incident. All hydrogen atoms were located in idealized positions and were treated with a riding model. All non-hydrogen atoms were assigned anisotropic thermal parameters. Refinements continued to convergence, using the recommended weighting schemes.

Dataset for **DIEA:Bipy** and **DIEA:Azopy** were collected on an Oxford Diffraction Xcalibur four-circle kappa geometry single-crystal diffractometer with Sapphire 3 CCD detector, using a graphite monochromated MoK α ($\lambda = 0.71073$ Å) radiation, and applying the CrysAlisPro Software system⁶ at 296 K. The crystal–detector distance was 45 mm.

Data reduction, including Lorentz and polarization corrections as well as absorption correction, was done by CrysAlis RED program.⁶ The structure was solved by Direct methods implemented in the SHELXS-2013 program.⁷ The coordinates and the anisotropic displacement parameters for all non-hydrogen atoms were refined by full-matrix least-squares methods based on F^2 using the SHELXL-2013 program.⁷

All hydrogen atoms were placed in geometrically idealized positions and constrained to ride on their carbon atom at distance 0.93 Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Table S1 Crystallographic data

Code	DIEA:Bipy	DIEA:Azopy	DIEA:BipyNO	DIEA:Bpe	DIEA:Bpen
Formula moiety	(C ₁₈ H ₈ I ₂) 2(C ₁₀ H ₈ N ₂)	(C ₁₈ H ₈ I ₂) 2(C ₁₀ H ₈ N ₄)	(C ₁₈ H ₈ I ₂) 2(C ₁₀ H ₈ N ₂ O)	(C ₁₈ H ₈ I ₂) (C ₁₂ H ₁₂ N ₂)	(C ₁₈ H ₈ I ₂) (C ₁₂ H ₁₀ N ₂)
Empirical formula	C ₃₈ H ₂₄ I ₂ N ₄	C ₃₈ H ₂₄ I ₂ N ₈	C ₃₈ H ₂₄ I ₂ N ₄ O ₂	C ₃₀ H ₂₀ I ₂ N ₂	C ₃₀ H ₁₈ I ₂ N ₂
Molecular weight	790.45	846.45	822.41	662.28	660.26
Color, Habit	yellow block	orange prism	orange prism	bronze prism	yellow plate
Crystal system	triclinic	monoclinic	triclinic	triclinic	monoclinic
Space group, Z	<i>P</i> -1, 2	<i>C</i> 2/c, 4	<i>P</i> -1, 2	<i>P</i> -1, 2	<i>P</i> 2 ₁ /c, 4
a, Å	9.7245(4)	16.0411(11)	9.6027(18)	9.5153(16)	14.4231(12)
b, Å	10.1191(4)	22.6435(11)	10.0523(19)	9.6261(16)	13.6011(11)
c, Å	17.5288(7)	9.6728(7)	18.021(4)	14.368(3)	13.4798(10)
α, °	87.839(3)	90.00	85.600(5)	96.346(5)	90.00
β, °	80.433(4)	102.322(7)	80.043(5)	93.215(5)	109.397(3)
γ, °	70.331(4)	90.00	68.603(5)	103.295(4)	90.00
Volume, Å³	2205.3(5)	3432.5(4)	1595.0(5)	1268.4(4)	2494.2(3)
Density, g/cm³	1.639	1.638	1.712	1.734	1.758
Temperature, °K	296(2)	296(2)	120(2)	120(2)	120(2)
Crystal size, min x mid x max	0.23 x 0.29 x 0.49	0.17 x 0.34 x 0.36	0.14 x 0.24 x 0.30	0.14 x 0.28 x 0.40	0.06 x 0.20 x 0.42
X-ray wavelength, Å	0.71073	0.71073	0.71073	0.71073	0.71073
μ, mm⁻¹	1.997	1.873	2.013	2.500	2.543
Absorption corr	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
Trans min / max	0.497 / 0.629	0.527 / 0.684	0.592 / 0.766	0.595 / 0.721	0.485 / 0.862
θ_{min}, °	4.17	4.13	2.176	2.192	2.117
θ_{max}, °	30.00	30.00	32.663	32.488	30.567
Reflections					
collected	16639	10609	45988	38542	28574
independent	9306	5009	10925	8522	7557
observed	6619	3363	10024	7891	4840
Threshold expression	>2σ(I)	>2σ(I)	I > 2σ(I)	I > 2σ(I)	I > 2σ(I)
R₁ (observed)	0.0382	0.0382	0.0375	0.0254	0.0580
wR₂ (all)	0.0782	0.0921	0.0948	0.0674	0.1619
Goodness of fit (all)	0.998	1.050	1.129	1.071	1.006
Δρ max / min	0.576 / -0.609	0.671 / -0.549	1.946 / -1.383	1.484 / -0.845	4.195 / -1.342
2θ limit	25.24	25.24	30.000	30.000	30.000
Completeness to 2θ limit	0.995	0.995	0.997	0.998	0.996

Table S2 Halogen bond geometries

Co-crystal	C–I ... N	I ... N (Å)	C – I ... N (°)
DIEA:Bipy	C(16)–I(1) ... N(1) ⁱ C	2.795(3)	179.4(1)
	(18)–I(2) ... N(3) ⁱⁱ	2.758(3)	178.0(1)
DIEA:Azopy	C(10)–I(1) ... N(1) ⁱⁱⁱ	2.805(3)	179.2(1)
DIEA:BipyNO	C(32)–I(1)–N(51)	2.709(3)	178.39(11)
	C(42)–I(2)–N(71)	2.778(3)	179.87(11)
DIEA:Bpe	C(32)–I(1)–N(51)	2.8088(18)	175.14(7)
DIEA:Bpen	C(32)–I(1)–N(51)	2.775(5)	176.07(18)
Symmetry code: (i) 1 – x, 1 – y, 1 – z; (ii) 1 – x, 2 – y, 1 – z; (iii) x, y – 1, z.			

S4. Stoichiometric control experiments

Three co-crystals which formed trimers instead of expected tetramers in initial solvent co-crystallization attempts (1:1 stoichiometry) were selected and co-crystallization experiments with two different stoichiometries (2:1 and 3:2) were conducted using Acetone as the solvent. The crystals obtained in each experiment were first analyzed with IR spectroscopy to identify the co-crystal formation and secondly these single crystals were analyzed using ¹H NMR spectroscopy to identify the respective stoichiometry of donor: acceptor. The results are summarized in the following table.

Table S3 Details and results of stoichiometric control experiments

Stoichiometry	Co-crystal	Outcome	IR analysis	¹ H NMR analysis
2:1	DIEA:Bipy	Crystals	Only DIEA	-
	DIEA:Azopy	Crystals	Only DIEA	-
	DIEA:BipyNO	Crystals	Only DIEA	-
3:2	DIEA:Bipy	Crystals	Co-crystals	1:2 stoichiometry (trimer) – see the ¹ H NMR (a) below
	DIEA:Azopy	Crystals	Only DIEA	-
	DIEA:BipyNO	Crystals	Only DIEA	-

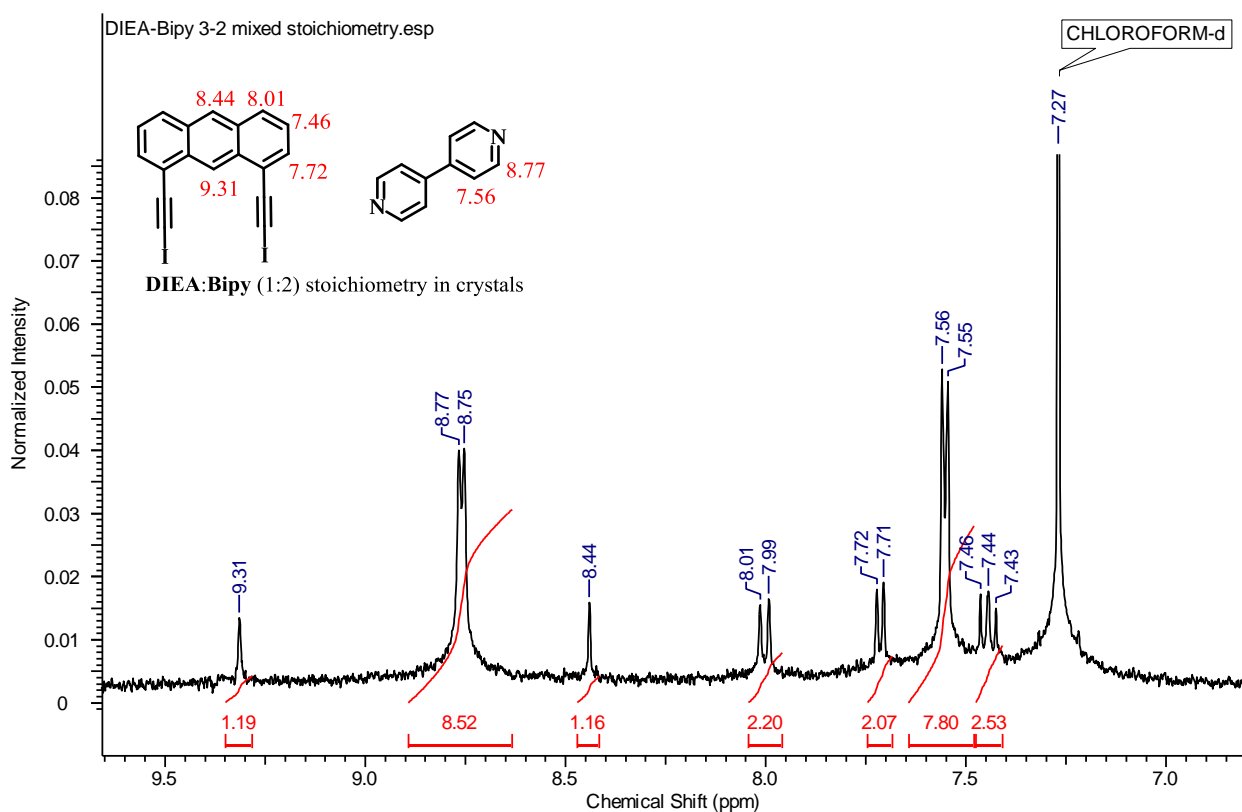


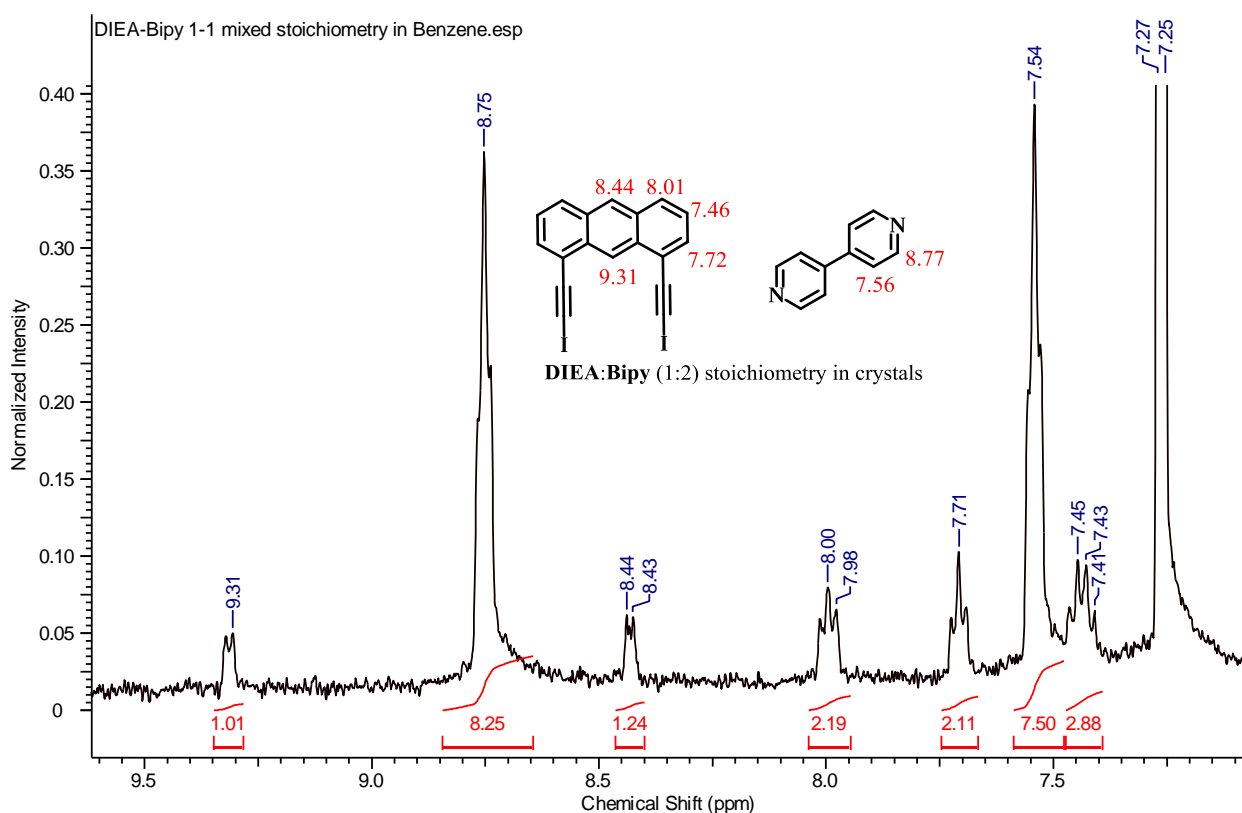
Figure S4 ^1H NMR of 1:2 stoichiometric co-crystal of **DIEA:Bipy**

S5. Solvent control experiments

As the change in stoichiometry did not yield the expected tetramer formation in **DIEA:Bipy**, **DIEA:Azopy** and **DIEA:BipyNO**, next attempts to convert these trimers to the molecular rectangles were conducted in different solvent systems using 1:1 stoichiometry between the donor: acceptor. First set of experiments were conducted with **DIEA:Bipy** co-crystal. With each selected solvent, a minute amount of acetone added initially in order to dissolve **DIEA** completely. As in the previous set of experiments, crystals obtained in each experiment were first analyzed with IR spectroscopy to identify the co-crystal formation and secondly these single crystals were analyzed using ^1H NMR spectroscopy to identify the respective stoichiometry of donor: acceptor. As only toluene yielded a 1:1 stoichiometric co-crystal of **DIEA:Bipy**, second set of experiments were conducted in toluene to obtain 1:1 co-crystals of **DIEA:Azopy** and **DIEA:BipyNO**. The results are summarized in the following table.

Table S4 Details and results of solvent control experiments

Solvent	Co-crystal	Outcome	IR analysis	¹ H NMR analysis
Acetonitrile	DIEA:Bipy	Precipitate	Only DIEA	-
Benzene	DIEA:Bipy	Crystals	Co-crystal	1:2 stoichiometry (trimer) – see the ¹ H NMR (b) below
Ethyl acetate	DIEA:Bipy	Crystals	Co-crystals	1:2 stoichiometry (trimer) – see the ¹ H NMR (c) below
Nitrobenzene	DIEA:Bipy	Precipitate	Only DIEA	-
Nitromethane	DIEA:Bipy	Precipitate	Only DIEA	-
Toluene	DIEA:Bipy	Crystals	Co-crystal	1:1 stoichiometry (tetramer)- see the ¹ H NMR (d) below
	DIEA:Azopy	Crystals	Co-crystal	1:2 stoichiometry (trimer) – see the ¹ H NMR (e) below
	DIEA:BipyNO	Precipitate	Only DIEA	-

**Figure S5** ¹H NMR of 1:2 stoichiometric co-crystal of **DIEA:Bipy** in benzene

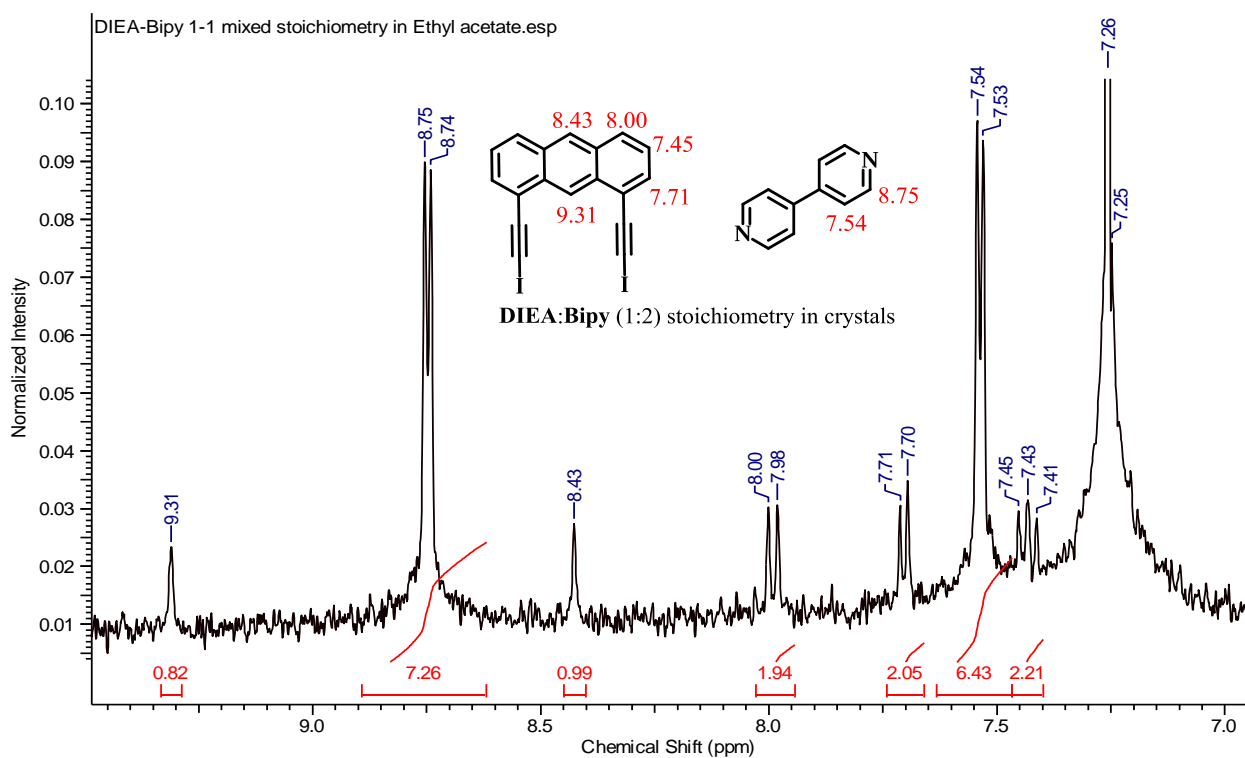


Figure S6 ^1H NMR of 1:2 stoichiometric co-crystal of **DIEA:Bipy** in ethyl acetate

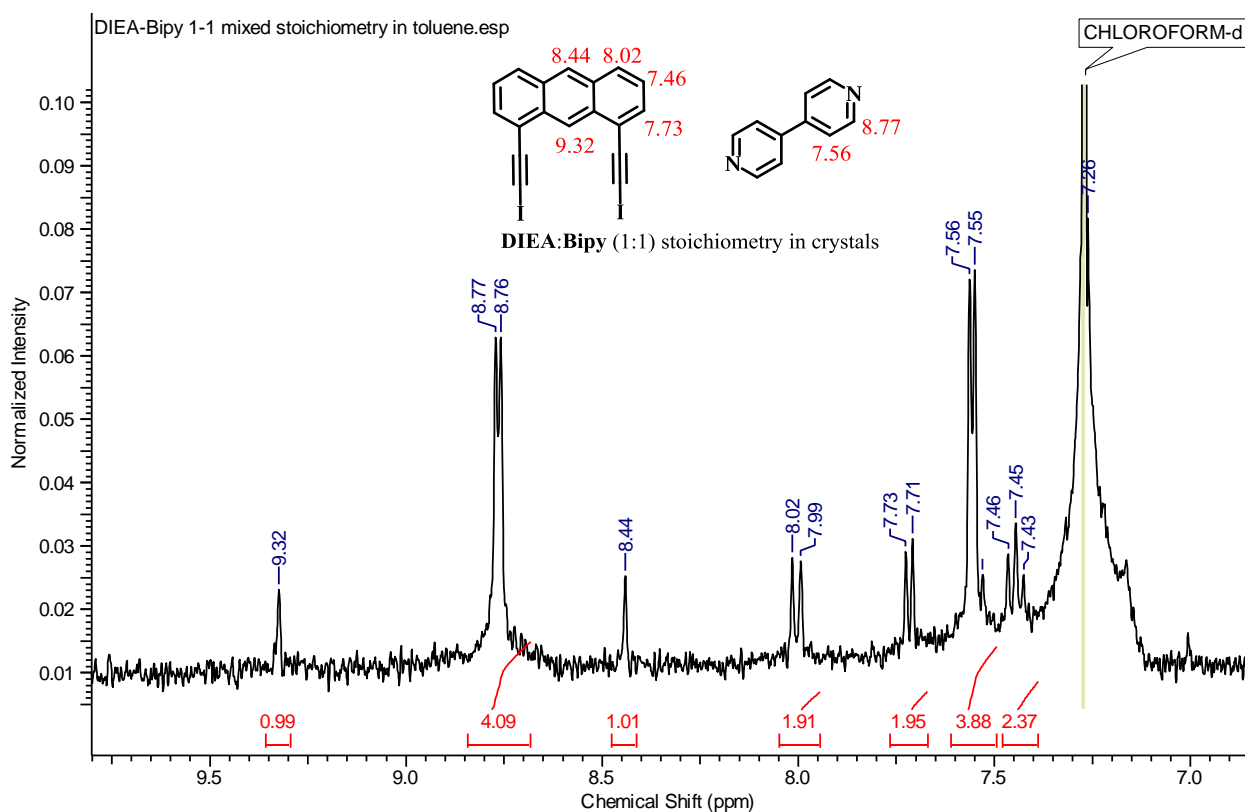


Figure S7 ^1H NMR of 1:1 stoichiometric co-crystal of **DIEA:Bipy** in toluene

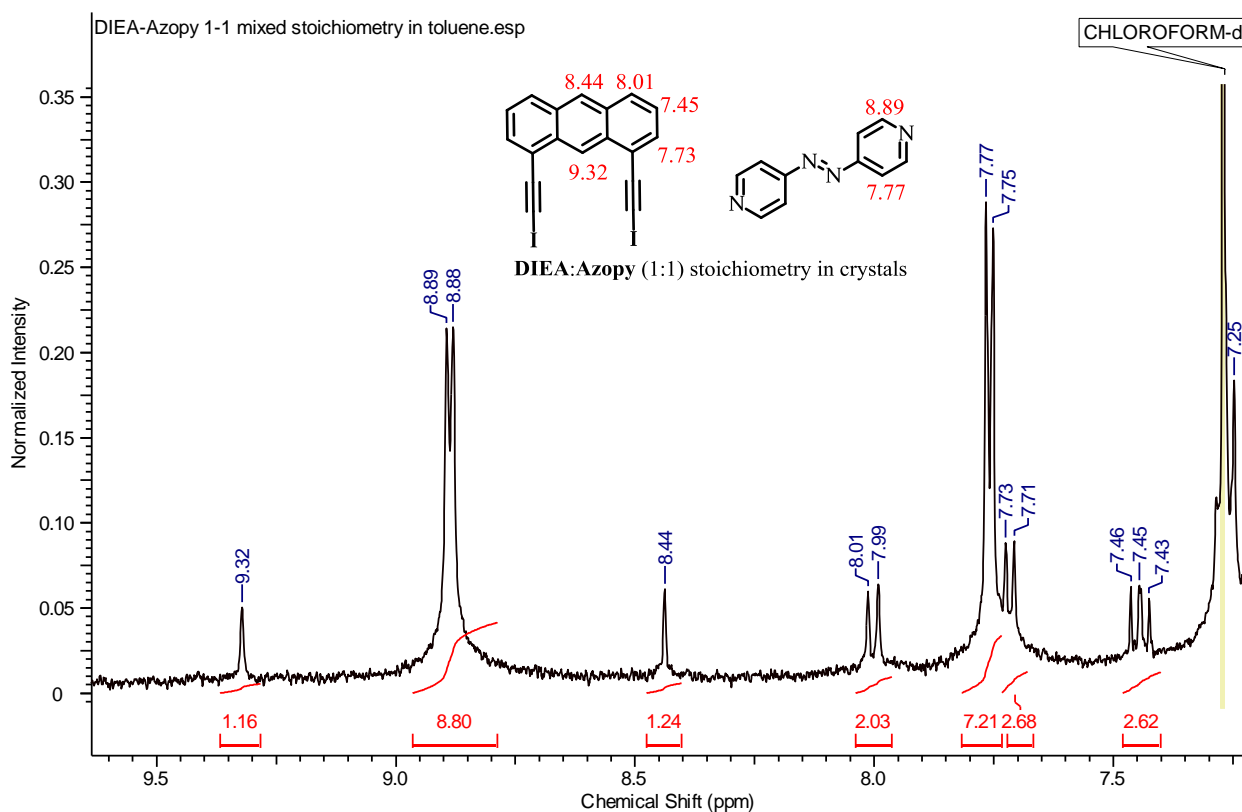


Figure S8 ^1H NMR of 1:2 stoichiometric co-crystal of **DIEA:Azopy** in toluene

References

- ¹. APEX2 v2013.10-0 (2013), Bruker Analytical X-ray Systems, Madison, WI.
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- ⁶. Oxford Diffraction, Xcalibur CCD System, CrysAlis Software System, Version 171.31, Oxford Diffraction Ltd. (2004).
- ⁷. Sheldrick, G. M. (2008). *Acta Crystallogr., Sect. A: Found. Crystallogr.* **A64**, 112–122.