Supporting Information for

Efficient Intramolecular Charge Transfer in Oligoyne-Linked D–π–A Molecular Wires

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Synthesis – Starting materials and instrumentation. *N*-(4-Ethynylphenyl)-*N,N*-diphenylamine (**6**)[1] and 1-bromo-2-trimethylsilylacetylene[2] were synthesized using reported methods. THF was purified from HPLC grade reagent using a commercial solvent purification system. Triethylamine (TEA) was dried over sodium metal and freshly distilled under argon before use. Flasks used to carry out Pd catalyzed reactions were flame-dried and the reactions were all protected with an argon atmosphere. Dichlorobis(triphenylphosphine)palladium(II) was prepared by the reported method.[3] Copper(I) iodide was used as purchased from Avocado (98%+ grade). ^{1}H and ^{13}C NMR spectra were recorded on a Brucker Avance-400 (400.13 MHz for ^{1}H and 100.61 MHz for ^{13}C), a Varian Unity-300 (299.95 MHz for ^{1}H and 75.42 MHz for ^{13}C) or a Varian Mercury-200 (199.99 MHz for ^{1}H and 50.29 MHz for ^{13}C) spectrometer, and the frequencies are quoted for each compound. Chemical shifts are quoted downfield from TMS. MS data were obtained using a Thermo Finnigan LTQFT instrument for ES low and high resolution mass, and a Micromass AutoSpec spectrometer operating at 70 eV for Electron Impact (EI). Elemental analyses were obtained on an Exeter Analytical Inc. CE-440 elemental analyzer. Melting points were measured in open-end capillaries using a Stuart Scientific SMP3 melting point apparatus. The temperatures at the melting points were ramped at 2.5 °C /min and were uncorrected.

1-[4-(*N,N*-Diphenylanimo)phenyl]-4-trimethylsilylbutadiyne (7). *N*-(4-Ethynylphenyl)-*N,N*-diphenylamine (**6**) (1.35 g, 5.0 mmol) and 1-bromo-2-trimethylsilylacetylene (1.03 g, 5.8 mmol) were dissolved in THF (5 mL). $Pd(PPh_3)_2Cl_2$ (0.18 g) and CuI (0.06 g) were added followed by triethylamine

(50 mL). The mixture was stirred at r.t. under Ar for 4 h to afford a thick yellow suspension. Diethyl ether (50 mL) was added and the mixture was suction filtered and the filtrate was evaporated under vacuum. The residue was column chromatographed on silica (eluent: hexane-DCM, 4:1 v/v) to afford **7** as a yellow solid (0.66 g, 36%): mp 158.0-158.9 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.24 (s, 9H), 6.95 (d, *J* = 8.8 Hz, 2H), 7.09 – 7.14 (m, 6H), 7.28 – 7.34 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) □δ -0.3, 73.4, 77.5, 88.3, 90.1, 113.3, 121.3, 124.0, 125.4, 129.5, 133.7, 146.8, 148.9; MS (EI) *m/z* 365 (M^+, 100%); HRMS (EI) calcd for $C_{25}H_{23}NSi$ 365.15998, found 365.15994.

[4-(*N,N*-Diphenylamino)phenyl]butadiyne (8). ***Caution:*** *The stability of terminal oligoynes is dependent on the nature of the end groups. Although no explosions were encountered during this work, great care should be taken when carrying out similar reactions.* To a solution of compound **7** (0.365 g, 1.0 mmol) in dry DCM (10 mL), dry methanol (10 mL) was added with stirring. Potassium carbonate powder (0.35 g) was added and the mixture was stirred at r.t. for 1 h to afford a yellow suspension. The solvents were removed by vacuum evaporation. DCM (10 mL) was added to the residue and the mixture was suction filtered and a yellow solid was obtained by vacuum evaporation of the filtrate (without heating). The crude product was purified on a silica column (eluent: hexane-DCM, 4:1 v/v) to afford **8** as pale yellow crystals (0.29 g, 99%): no m.p. was observed <350 ^{o}C by heating a crystal at 5 ^{o}C /min. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.48 (s, 1H), 6.95 (d, *J* = 8.8 Hz, 2H), 7.08 – 7.13 (m, 6H), 7.28 – 7.36 (m, 6H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 68.5, 71.0, 72.7, 76.0, 112.8, 121.2, 124.1, 125.4, 129.5, 133.8, 146.8, 149.0. Anal. Calcd for $C_{22}H_{15}N$: C, 90.07; H, 5.15; N, 4.77; Found: C, 90.12; H, 5.14; N, 4.81. A single crystal for X-ray analysis was prepared by slow evaporation of its solution in hexane-DCM mixture.

2-(4-*tert*-Butylphenyl)-5-(4-bromobutadiynylphenyl)-1,3,4-oxadiazole (10). ***Caution:*** *The stability of terminal oligoynes is dependent on the nature of the end groups. Although no explosions were encountered during this work, great care should be taken when carrying out similar reactions.* To a solution of **9**[4] (0.65 g, 2.0 mmol) in acetone (40 mL, AR grade), were added *N*-bromosuccinimide (0.53 g, 3.0 mmol) and silver nitrate (50 mg). The mixture was stirred at r.t. for 1 h to afford a milky-yellow suspension. The solvent was removed by vacuum evaporation and the yellow solid residue was purified on a silica column (eluent DCM-diethyl ether, 95:5 v/v) to afford **10** as a yellow solid (0.73 g, 90%): mp: 138 ^{o}C, when the sample in a capillary tube was inserted into the preheated heating element. (However, gradually heating the solid at <10 ^{o}C/min led to the formation of a black tar solid which did not melt <350 ^{o}C); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.36 (s, 1H), 7.54 (d, *J* = 8.8 Hz, 2H), 7.62, (d, *J* = 8.4 Hz, 2H), 8.04 (d, *J* = 8.8 Hz, 2H), 8.07 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 31.1, 35.1, 46.4, 65.1, 72.9, 76.9, 120.8, 124.3, 124.4, 126.0, 126.7, 126.8, 133.4, 155.6, 163.6, 164.9. MS (EI) *m/z* 404 (M^+, 90%), 406 (M^+, 100%); HRMS (EI) calcd. for $C_{22}H_{17}BrN_2O$ 404.05243, found 404.05240.

2-(4-*tert*-Butylphenyl)-5-{4-[4-(*N*,*N*-diphenylamino)phenyl]hexatriynylphenyl}-1,3,4-oxadiazole (3).To the solution of **6** (0.16 g, 0.60 mmol) and **10** (0.203 g, 0.50 mmol) in dry THF (5 mL) were added $Pd(PPh_3)_2Cl_2$ (20 mg) and copper(I) iodide (10 mg), followed by triethylamine (15 mL). The mixture was stirred under argon at r.t. for 3 h to yield a reddish-brown suspension. The mixture was evaporated to dryness under vacuum and the solid residue was purified on a silica column (eluent: DCM-diethyl ether 95:5 v/v) to afford **3** as a yellow solid (0.167 g, 56%): mp 204.9-206.3 ^oC; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.39 (s, 9H), 6.93 (d, *J* = 8.8 Hz, 2H), 7.12 (d, *J* = 8.6 Hz, 6H), 7.29 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.6 Hz, 2H), 7.36 (d, *J* = 8.8 Hz, 2H), 7.56 (d, *J* = 8.6 Hz, 2H), 7.66 (d, *J* = 8.8 Hz, 2H), 8.06 (d, *J* = 8.6 Hz, 2H), 8.10 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 31.1, 35.1, 66.0, 68.6, 73.7, 77.39, 77.42, 80.5, 112.1, 120.8, 120.9, 124.3, 124.4, 124.5, 124.6, 126.1, 126.7, 126.8, 129.5, 133.4, 134.1, 146.5, 149.3, 155.5, 163.6, 164.9; MS (EI) *m/z* 593 (M^+, 100%); HRMS (EI) calcd. for $C_{42}H_{31}N_3O$ 593.24671, found 593.24669. Yellow needles suitable for X-ray structural analysis were obtained by slow evaporation of a solution of the solid in DCM-methanol mixture.

2-(4-*tert*-Butylphenyl)-5-{4-[4-(*N*,*N*-diphenylamino)phenyl]octatetraynylphenyl}-1,3,4-oxadiazole (4). By analogy with the synthesis and purification of **3**, the reaction of **10** (0.203 g, 0.50 mmol) with **8** (0.220 g, 0.75 mmol) in the presence of $Pd(PPh_3)_2Cl_2$ (20 mg) and copper(I) iodide (10 mg), in THF (5 mL) and triethylamine (15 mL) afforded **4** as an orange solid (0.12 g, 39%): mp ca 201 ^oC when heated at 10 ^oC/min (no mp was observed <350 ^oC when a sample was heated at 2.5 ^oC/min); ^1H NMR ($CDCl_3$, 400 MHz) δ 1.38 (s, 9H), 6.92 (d, *J* = 9.0 Hz, 2H), 7.12 (m, 6H), 7.30 (m, 4H), 7.35(d, *J* = 8.8 Hz, 2H), 7.55 (d, *J* = 8.8 Hz, 2H), 7.67 (d, *J* = 8.8 Hz, 2H), 8.06 (d, *J* = 8.8 Hz, 2H), 8.11 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 31.3, 35.4, 63.5, 65.5, 67.3, 69.3, 74.1, 76.7, 77.5, 79.6, 111.7, 120.9, 121.1, 124.3, 124.7, 125.0, 126.0, 126.3, 127.0, 127.1, 129.8, 133.9, 134.6, 146.7, 149.8, 155.9, 163.8, 165.3. MS (EI) *m/z* 617 (M^+, 100%); HRMS (EI) calcd for $C_{44}H_{31}N_3O$ 617.24671, found 617.24670. Orange prisms for X-ray structural analysis were obtained by slow evaporation of a DCM-hexane solution.

4-(*N*,*N*-Diphenylamino)phenyl-4'-(3-hydroxy-3-methyl)butynylbiphenyl (13). 4-Bromo-4'-(*N*,*N*-diphenylamino)biphenyl (**12**) was synthesized in 71% yield using a literature method[5] by reacting 4-bromo-4'-iodobiphenyl with diphenylamine. A mixture of **12** (2.00 g, 5.0 mmol), 2-methyl-3-butyn-2-ol (2.10 g, 25 mmol), $Pd(PPh_3)_2Cl_2$ (180 mg) and copper(I) iodide (60 mg) in piperidine (20 mL) was stirred at 50 ^oC for 3 h and then at 60 ^oC for an additional 1 h. The solution was evaporated to dryness under vacuum (*Caution: carry out in a fume cupboard due to the toxicity of piperidine*). The dark yellow oily residue was purified on a silica column (eluent: DCM-diethylether, 9:1 v/v) to afford **13** as a pale yellow amorphous solid (2.00 g, 99%): mp 76.0-78.0 ^{o}C; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 1.82 (s, 6H), 3.24 (s, 1H), 7.15 (t, *J* = 7.2 Hz, 2H), 7.25 (m, 6H), 7.37 (t, *J* = 7.7 Hz, 4H), 7.55 (d, *J* = 8.5 Hz, 2H), 7.60 (s, 4H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 31.3, 65.3, 81.9, 94.4, 120.9, 122.9, 123.4, 124.3, 126.0, 127.4, 129.1, 131.9, 133.6, 139.9, 147.2, 147.3; MS (EI) *m/z* 403 (M$^+$, 100%); HRMS (EI) calcd for $C_{29}H_{25}NO$ 403.19361, found 403.19359.

4-(*N,N*-Diphenylamino)phenyl-4'-ethynylbiphenyl (14). A mixture of **13** (2.00 g, 4.96 mmol) and sodium hydroxide powder (1.0 g) in dry toluene (30 mL) was refluxed for 1.5 h under argon. Toluene was removed under vacuum and the residue was purified on a silica column (eluent: hexane-DCM, 2:1 v/v) to afford **14** as pale yellow crystals (1.20 g, 70%): mp 164.0-165.0 ^{o}C; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 3.13 (s, 1H), 7.06 (t, *J* = 7.3 Hz, 2H), 7.15 (m, 6H), 7.28 (d, *J* = 7.6 Hz, 2H), 7.30 (d, *J* = 7.3 Hz, 2H), 7.48 (d, *J* = 8.2 Hz, 2H), 7.55 (s, 4H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 77.6, 83.7, 120.4, 123.1, 123.6, 124.6, 126.4, 127.7, 129.3, 132.5, 133.8, 141.0, 147.6, 147.7. MS (EI) *m/z* 345 (M$^+$, 100%); HRMS (EI) calcd for $C_{26}H_{19}N$ 345.15175, found 345.15179.

2-(4-*tert*-Butylphenyl)-5-{4,-[4'-(*N,N*-diphenylamino)biphenyl]hexatriynylphenyl}-1,3,4-oxadiazole (5). By analogy with the synthesis and purification of **3**, the reaction of **14** (0.181 g, 0.524 mmol) with **10** (0.203 g, 0.5 mmol) in the presence of Pd(PPh$_3$)$_2$Cl$_2$ (20 mg) and copper(I) iodide (10 mg), in a mixture of THF (5 mL) and triethylamine (15 mL) afforded **5** as a yellow solid (0.13 g, 42%): mp 224.2 – 225.0 ^{o}C; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 1.39 (s, 9H), 7.07 (t, *J* = 7.3 Hz, 2H), 7.15 (m, 6H), 7.30 (m, 4H), 7.48 (d, *J* = 8.6 Hz, 2H), 7.58 (m, 6H), 7.70 (d, *J* = 8.6 Hz, 2H), 8.08 (d, *J* = 8.6 Hz, 2H), 8.13 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR (CDCl$_3$, 50 MHz) δ 31.1, 35.1, 66.3, 68.2, 74.9, 77.2, 77.6, 79.7, 118.8, 120.9, 123.30, 123.33, 124.4, 124.6, 124.7, 126.1, 126.5, 126.8, 126.9, 127.7, 129.3, 133.2, 133.5, 142.0, 147.4, 148.0, 155.6, 163.6, 165.0. MS (EI) *m/z* 669 (M$^+$, 100%); HRMS (EI) calcd for $C_{48}H_{35}N_3O$ 669.27801, found 669.27800. A yellow plate for X-ray structural analysis was obtained by slow evaporation of a DCM solution of the compound.

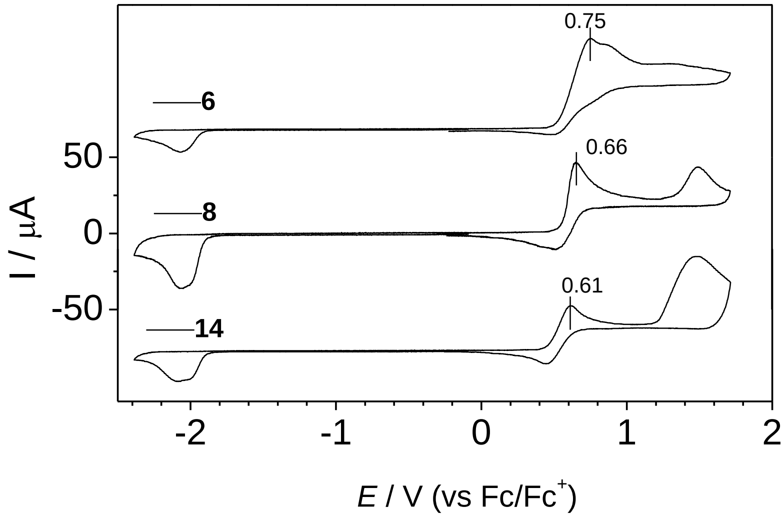


Figure S1. Cyclic voltammograms of compounds **6**, **8** and **14** in MeCN. All of the solutions contained TBAPF$_6$ (0.1 M) as the supporting electrolyte, scan rate 100 mV/sec, using Pt disk (Φ 1.8 mm) as the working electrode, Pt wire as the counter electrode and Ag/AgNO$_3$-MeCN as the reference electrode.

Steady state optical spectroscopy. Absorption spectra were measured on a Perkin Elmer Lambda 19™ spectrophotometer and photoluminescence data were obtained using a Jobin Yvon Horiba Fluoromax 2™. The optical density (OD) in the luminescence measurements was in the range 0.10 – 0.15. The photoluminescence quantum yield (PLQY) was measured using an integrating sphere as outlined by Porres et al.[6] For the low temperature PL measurements an Oxford DN 74 liquid nitrogen cryostat was used.

Time-resolved photoluminescence. The time-resolved luminescence was measured using the standard time correlated single photon counting technique (TCSPC)[7] with modifications as follows. The excitation source consisted of a mode-locked cavity dumped (APE™ Pulse switch) Ti:Sapphire laser (MIRA™, Coherent). Near infrared optical pulses with a temporal width of ~200 fs (FWHM) were used to generate the 3rd harmonic UV pulses at a wavelength of ~300 nm with an Inrad™ (Model 5-050) harmonic generator. The fluorescence was detected using a photomultiplier tube (id Qunatic™ Model id 100-50) linked to a time-to-amplitude converter (Ortec™ 567) and multichannel analyzer (E.G. & G™. Trump Card and Maestro for Windows v. 5.10). The instrument response function (IRF) of the apparatus was measured from the scattered light, giving an IRF with a duration of 125 ps FWHM. All fluorescence decays were recorded to a minimum of 10,000 counts in the peak channel of the pulse height analyzer. The data was analyzed using the standard method of iterative reconvolution and nonlinear least squares fitting in a Microsoft Excel spreadsheet.[8] The quality of the calculated fits was judged using statistical parameters, including the Durbin-Watson parameter, reduced chi-squared, random residuals and auto correlated residuals. The experimental data was subsequently fitted to a sum of exponentials:

$$F(\lambda,t)=\sum_i A_i(\lambda)\cdot\exp\left(-\frac{t}{\tau_i}\right)$$

Two photon excitation luminescence. TPA measurements have been outlined by Webb *et al.*[9] In this approach the ratio of the reference and sample TPE-PL is given by:

$$\frac{\sigma_2^S\cdot\phi^S}{\sigma_2^R\cdot\phi^R}=\frac{C_R\cdot n_S\cdot F^S(\lambda)}{C_S\cdot n_R\cdot F^R(\lambda)}$$

where ϕ is the total emission quantum yield of the compound for sample and reference, C is the concentration, n the refractive index and $F(\lambda)$ is the integrated PL spectrum. The experimental procedures used have been described in a previously.[10] Briefly, the TPE source consisted of a mode-locked cavity dumped (APE™ Pulse switch) Ti:Sapphire laser (MIRA™, Coherent) producing near infra red optical pulses with a temporal width of ~150 fs (FWHM) in the wavelength range 740 – 810 nm, and a repetition rate of 4 MHz. The excitation light was focused into the sample solution using an Olympus LWD C A20 (20x) objective. The emission was subsequently collected using a dichroic mirror (Semrock FF735) and detected using a fiber coupled CCD spectrograph (Avantes Avaspec 2048FT) with a 100 μm core fibre. The laser power was monitored using a photodiode with a known response curve, calibrated against a free standing power meter. The intensity of the excitation light was varied using a variable ND filter (Edmund Optics) mounted on a translation stage. The typical average excitation power was 5-50 mW corresponding to pulse energies of 1.25 – 12.5 nJ/pulse. Spectra from the CCD spectrograph were corrected for background and spectral response.

Ultrafast transient absorption spectroscopy. Femtosecond transient absorption measurements of the ground state recovery were made with a conventional single wavelength pump probe set up. Briefly, this comprised a Coherent Mira 900-F Ti:Sapphire oscillator and a Coherent RegA 9000 Ti:Sapphire regenerative amplifier providing pulses of approximately 180 fs with a repetition rate of 100 kHz at 780 nm. The pulses were frequency doubled by a BBO crystal within a Coherent OPA-9000 optical parametric amplifier, yielding pulses of up to 1 μJ at 390 nm. The 390 nm laser pulses were split to provide both pump and probe pulses at the same wavelength, the probe pulse was delayed optically using a Newport IMS-600 delay stage and both were then loosely focused through the sample in a quartz cuvette. The relative change in transmission of the probe beam was measured using a silicon photodiode with standard lockin techniques.

X-ray crystallography.

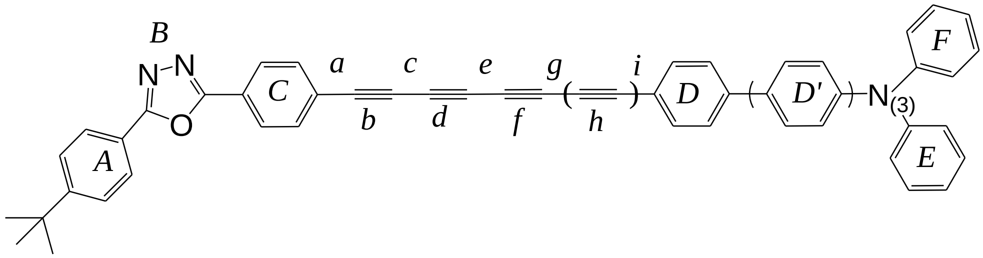
Single-crystal diffraction experiments (Table S1) were carried out on a SMART 3-circle diffractometers with CCD area detectors 1K (for **3, 8**) or 6K (for **4**, **5**), using graphite-monochromated Mo-K_α radiation (λ=0.71073 Å) and Cryostream (Oxford Cryosystems) open-flow N_2 cryostats. The structures were solved by direct methods and refined by full-matrix least squares against F^2 of all data, using SHELXTL 6.14 software (Bruker AXS, Madison, WI, USA, 2003). The diffraction of **4** was weak (mean $I/\sigma(I)=4.5$) due to small crystal size, hence low precision. In **5**, the *t*-Bu group is rotationally disordered between two orientations with occupancies 93% and 7%. The main position (84%) of the DCM molecule is such that the two chlorine atoms [Cl(1) and Cl(1')] are related via an inversion center, and the carbon atom is disordered between two positions related via this center. The remaining 16% of the DCM molecule is distributed between two other inversion-related positions. Structure **8** (Fig S2) does not contain the usual ≡C–H…π(C≡C) hydrogen bonds, the shortest contacts ≡C–H…C(Ph) of 2.91 to 3.06 Å (for the C–H bond distance normalized to 1.08 Å) exceeding the sum of the van der Waals radii (2.88 Å).[11]

Table S1. Crystal data.

Compound	**3**	**4**	**5**	**8**
CCDC dep. no.	702641	701642	701643	701644
Formula	$C_{42}H_{31}N_3O$	$C_{44}H_{31}N_3O$	$C_{48}H_{35}N_3O\cdot\frac{1}{2}CH_2Cl_2$	$C_{22}H_{15}N$
Formula weight	593.70	617.72	712.25	293.35
T, K	120	120	120	120
Symmetry	triclinic	triclinic	triclinic	triclinic
Space group	$P\bar{1}$ (# 2)	$P\bar{1}$ (# 2)	$P\bar{1}$ (# 2)	$P\bar{1}$ (# 2)
a, Å	8.4696(9)	8.0926(7)	9.5789(5)	8.1846(8)
b, Å	12.9559(15)	11.9612(10)	12.2322(7)	10.3429(10)
c, Å	14.7935(18)	18.1669(15)	16.4942(9)	10.5085(10)
α, °	87.621(5)	108.52(1)	105.789(9)	64.624(8)
β, °	87.206(6)	93.64(1)	91.282(9)	88.993(9)
γ, °	77.005(4)	93.63(1)	90.973(10)	89.307(8)

V, Å^3	1579.1(3)	1657.6(3)	1858.7(3)	803.58(13)
Z	2	2	2	2
μ, mm^{-1}	0.08	0.07	0.15	0.07
Refls collected	14114	9821	25823	8760
Unique refls	7174	5839	10800	3676
R_{int}	0.099	0.075	0.044	0.029
Refls $F^2>2\sigma(F^2)$	3105	3326	6594	3004
$R[F^2>2\sigma(F^2)]$	0.095	0.081	0.049	0.038
w$R(F^2)$, all data	0.283	0.149	0.128	0.100

Table S2. Selected bond distances (Å) and dihedral angles (º)



	3	**4**	**5**	**8**
a	1.431(6)	1.427(5)	1.433(2)	
b	1.211(6)	1.201(5)	1.204(2)	
c	1.360(6)	1.370(5)	1.368(2)	
d	1.205(6)	1.208(5)	1.210(2)	
e	1.356(6)	1.356(5)	1.370(2)	
f	1.205(6)	1.216(5)	1.206(2)	1.1902(18)
g		1.363(5)		1.3780(16)
h		1.198(5)		1.2049(16)
i	1.445(7)	1.431(5)	1.434(2)	1.4274(15)
Oligoyne bend (º)	27.6	13.9	3.8	8.7
A/B	23.9	4.7	3.5	
B/C	15.4	8.9	11.6	
C/D (D/D')	23.0	19.3	21.8 (37.1)	
D/N(3)*	38.8	37.1	58.7	22.5
N(3)/*E*	56.8	56.9	40.5	65.4

N(3)/*F*	27.3	27.1	35.6	34.9

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[*] The bonding plane of N(3), drawn through this atom and three adjacent carbon atoms

In molecule **8** the N atom is planar-trigonal, benzene rings *D*, *E* and *F* are inclined to its plane by 22.5, 65.4 and 34.9°, respectively, in a propeller-like fashion. The bond distances N-C(*D*) 1.4009(14), N-C(*E*) 1.4364(14) and N-C(*F*) 1.4197(14) Å inversely correlate with these angles, reflecting the degree of π-conjugation. Ring *D* shows a significant quinoid distortion: the C(2)-C(3) and C(5)-C(6) bonds average 1.3797(16) Å, compared to 1.4024(16) Å for the remaining four bonds.

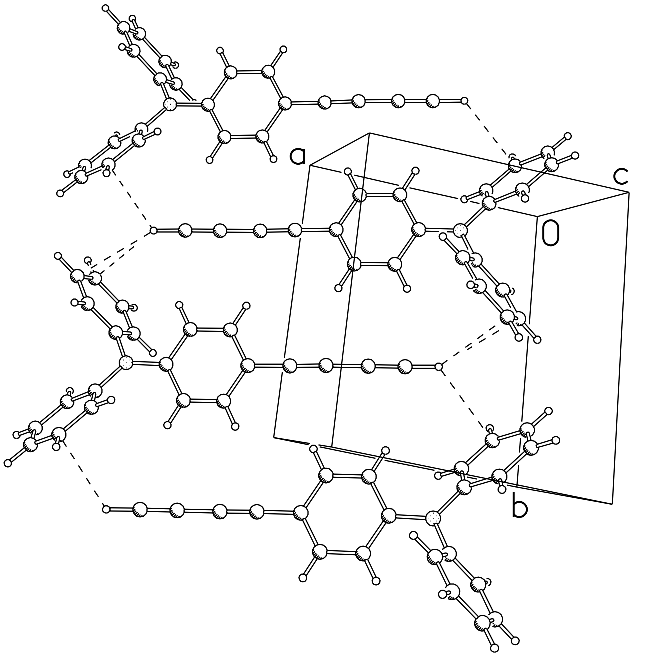

Figure S2. Crystal packing of **8**, showing intermolecular ≡C–H…C contacts (dashed lines).

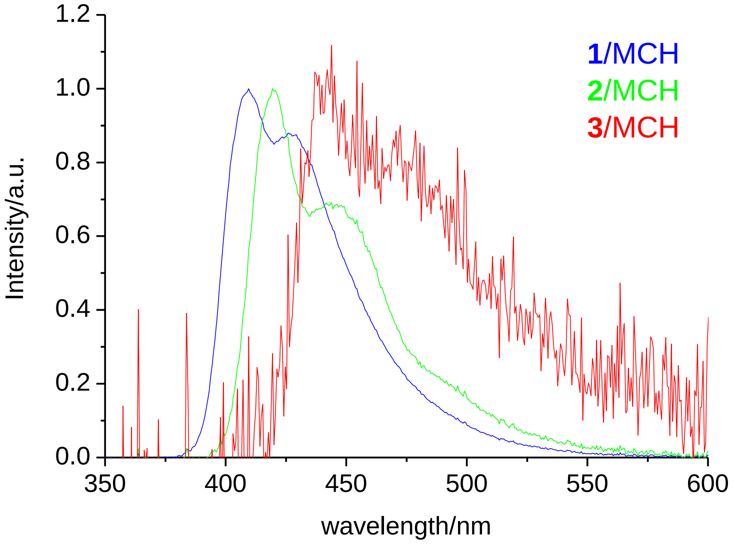

Figure S3. Two photon excited emission spectra for **1**, **2**, and **3** for excitation at 790 nm. All spectra have been normalized to a similar intensity scale in arbitrary units.

Figure S4 shows the excited state absorption spectra of **3** and **4** in MCH. These experiments where performed as outlined previuosly.[11] The maximum of the absorption band is at ca. 475 nm for **3** and 460 nm for **4**. Both systems exhibit a tail into the red; however, for **3** there is no measurable absorption beyond 700 nm and for **4** the corresponding point is at ca. 600 nm. Figure S4 shows pump and probe for excitation at 355 nm with a Q-switched YAG (EKSMA) and probe with a CW laser at 639 nm. The corresponding experiment probing at 470 nm did not result in any detectable signal. The time-resolution in these experiments is ca. 70 ns. Hence we conclude that the absorption recovery of the excited state bands of **3** and **4** is in the order of 10 ns. The recovery signal could be fitted to a single exponential model and the data is summarized in Table S3.

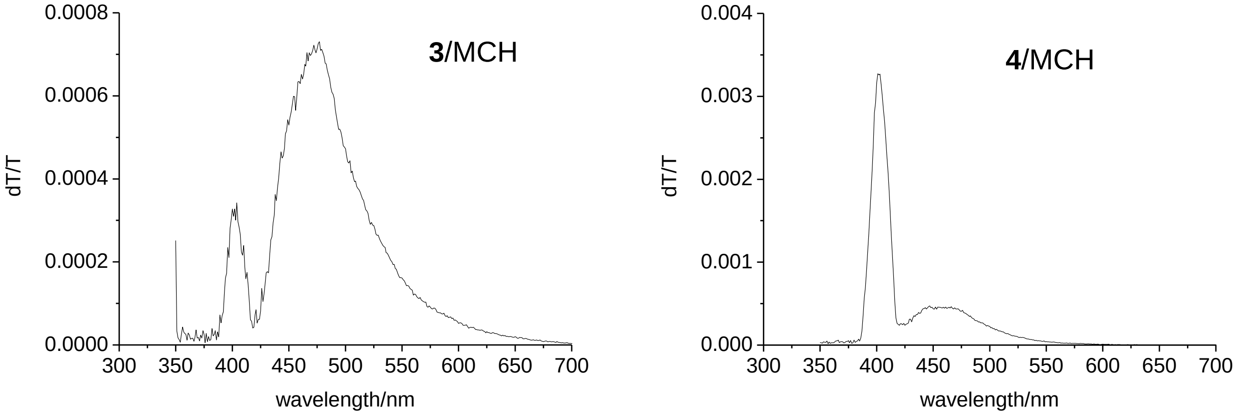

Figure S4. Excited state absorption for compounds **3** and **4,** for excitation at 400 nm. The sharp peak in the spectra at 400 nm is scattered light from the excitation source.

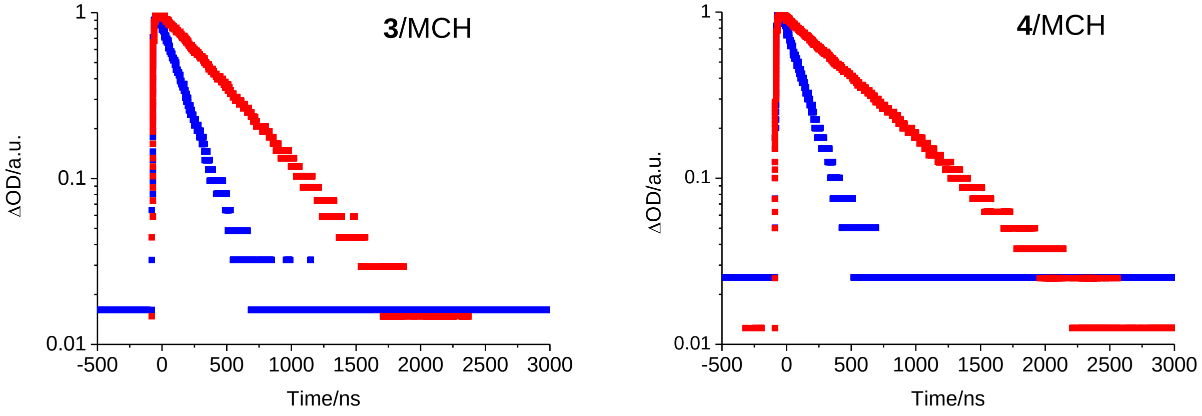

Figure S5. Pump and probe measurements of **3** and **4** in methylcyclohexane for excitation at 355 nm and probe at 639 nm. For both systems, data in blue are for an oxygenated solution and data in red are for a solution that has been degassed using nitrogen for several min. See Table S3 for details.

Table S3. Analysis of the absorption recovery experiments. See text for details.

Compound	Aerated solution: recovery time/ns	Degassed solution: recovery time/ns
3/MCH	187	504
4/MCH	169	613

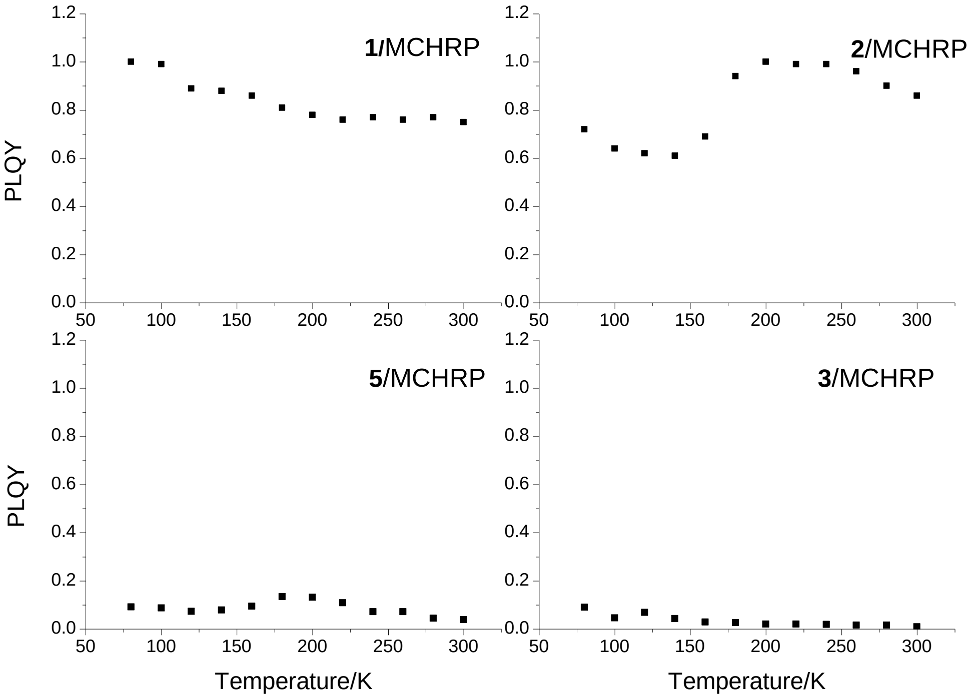

Figure S5. Temperature dependent PLQY data for compounds **1**, **2**, **3** and **5** in a medium consisting of methylcyclohexane and isopentane (4:1 v/v) (MCHRP). This is a non-polar host which forms a glass at low temperature.

References for the Supporting Information

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