Supporting Information for

Intramolecular Singlet Fission in a Face-to-Face Stacked Tetracene Trimer

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1. The crystal structure of dimer 3

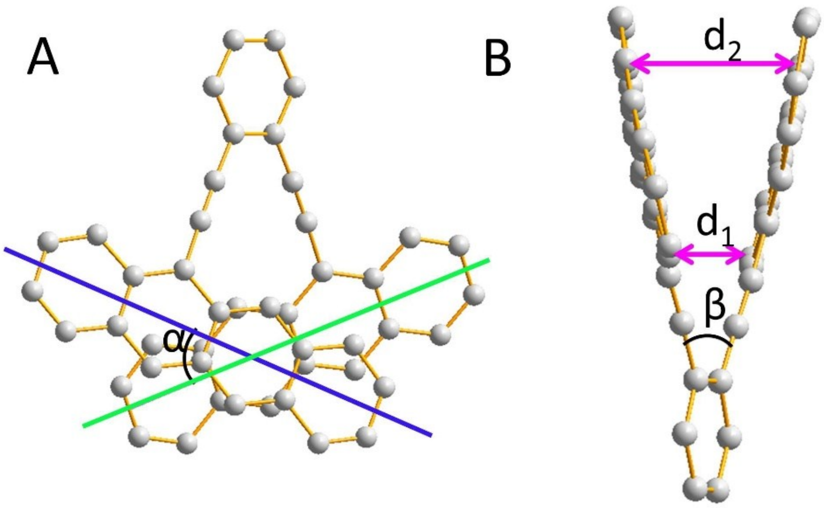

Figure S1. The crystal structure of dimer **3**.[S1]

Table S1. The comparison of the structural parameters between the minimized structure and the crystal structure.[S1]

	α (α_1=α_2)	β (β_1=β_2)	d_1 (Å)	d_2 (Å)
Dimer **3** (crystal structure)	44.7°	22.8°	3.1	3.8
Dimer **3** (minimized molecular structure)	41.5°	11.6°	3.1	3.8

2. The absorption spectra of trimer 4 and the superposition of dimer 3 and monomer 2

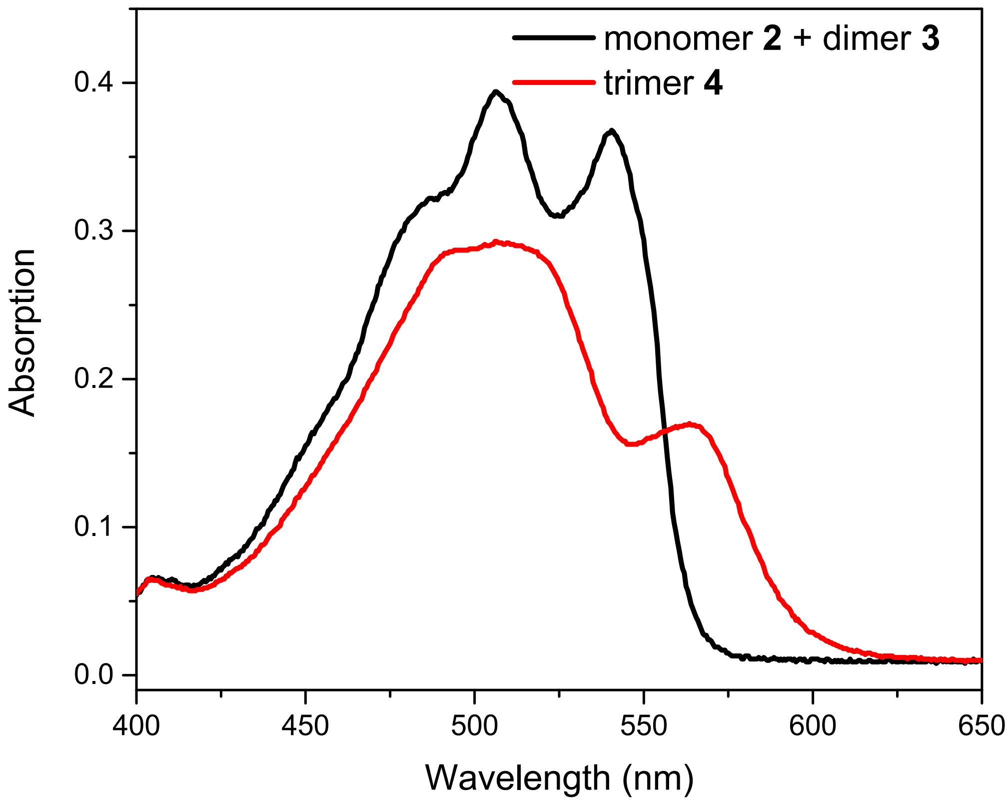

Figure S2. The absorption spectra of trimer **4** and the superposition of dimer **3** and monomer **2**.

3. **The absorption spectra of trimer 4 and the superposition of monomer 1 and monomer 2**

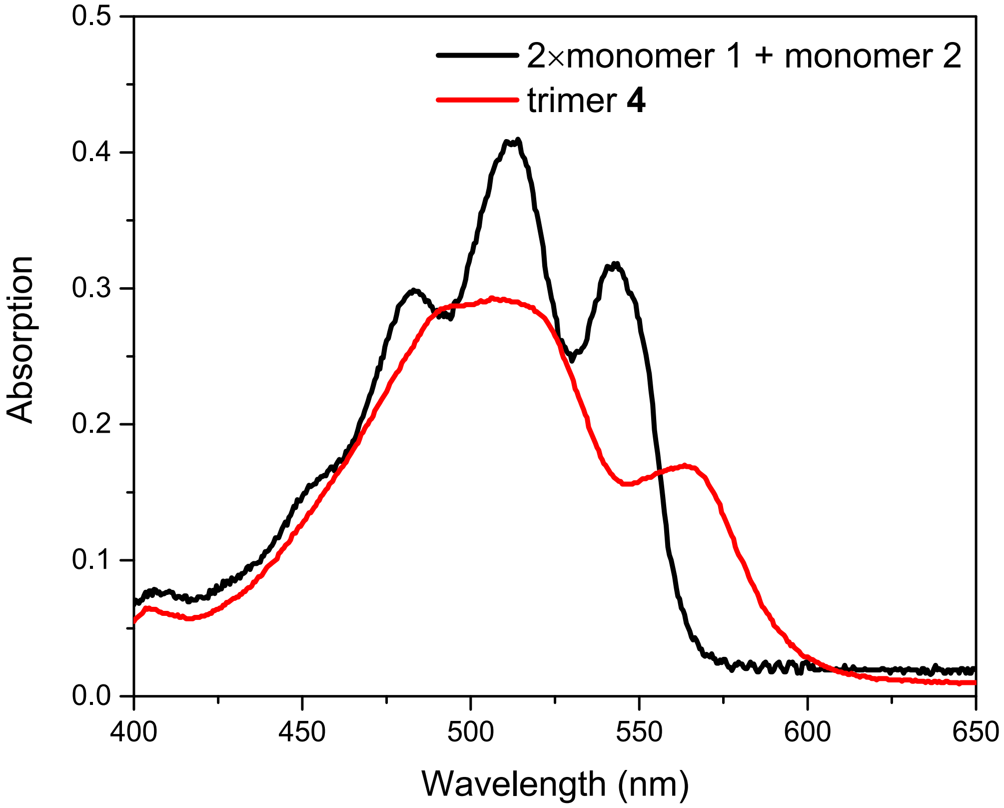

Figure S3. The absorption spectra of trimer **4** and the superposition of monomer **1** and monomer **2**.

4. Electronic orbitals (HOMO and LUMO) for the ground state (S_0) of dimer 3 and trimer 4

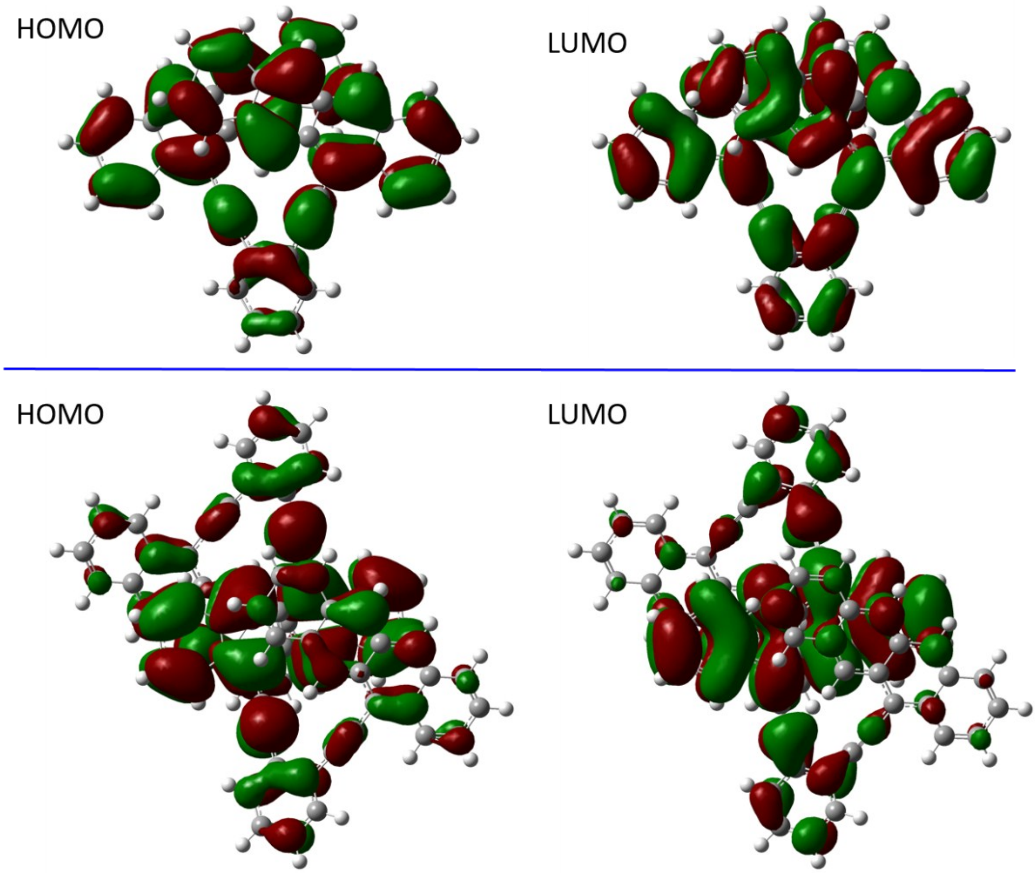

Figure S4. Electronic orbitals (HOMO and LUMO) for the ground state (S_0) of dimer **3** (top) and trimer **4** (below).

5. The transient absorption of dimer 3

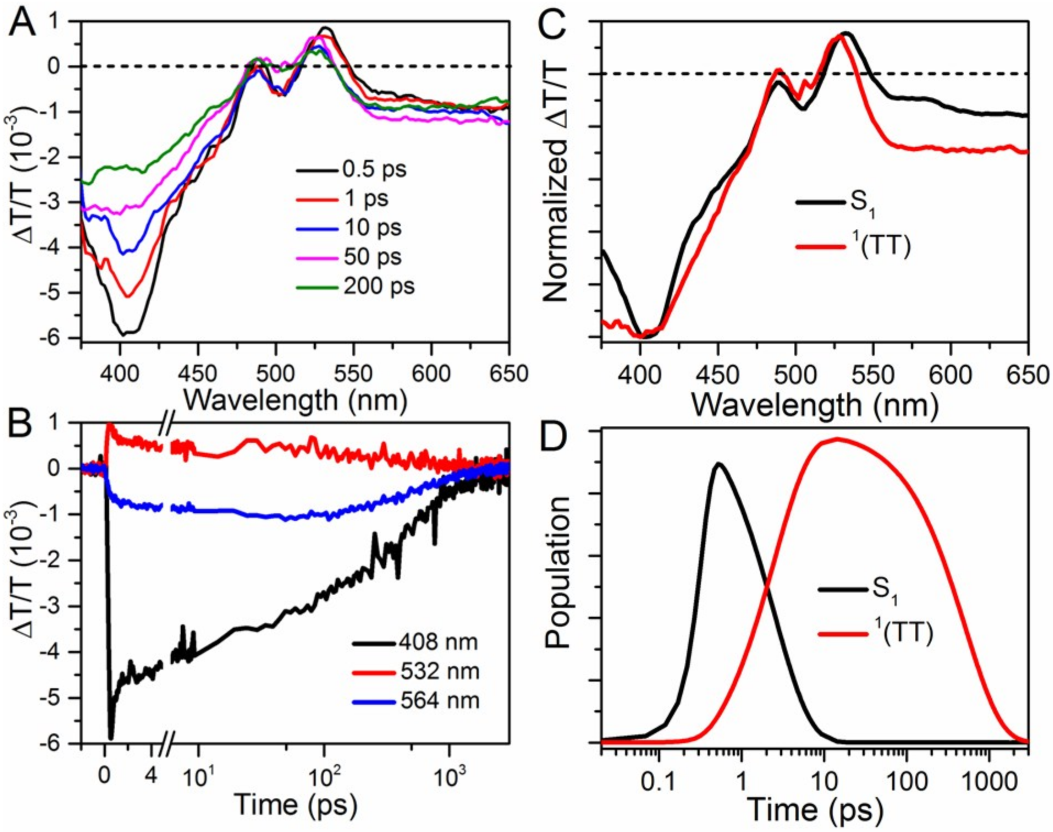

Figure S5. A) The transient absorption spectra of dimer **3** in degassed THF (5×10^{-5} M) with the excitation wavelength at 500 nm. B) The transient absorption dynamics of dimer **3** probed at different wavelengths. C) Deconvoluted transient spectra of singlet (S_1) and triplet pair (^{1}(TT)) of dimer **3** as solved by global analysis. D) Population evolution of dimer **3** obtained from global analysis.

6. The sensitized experiment of trimer 4 in degassed THF

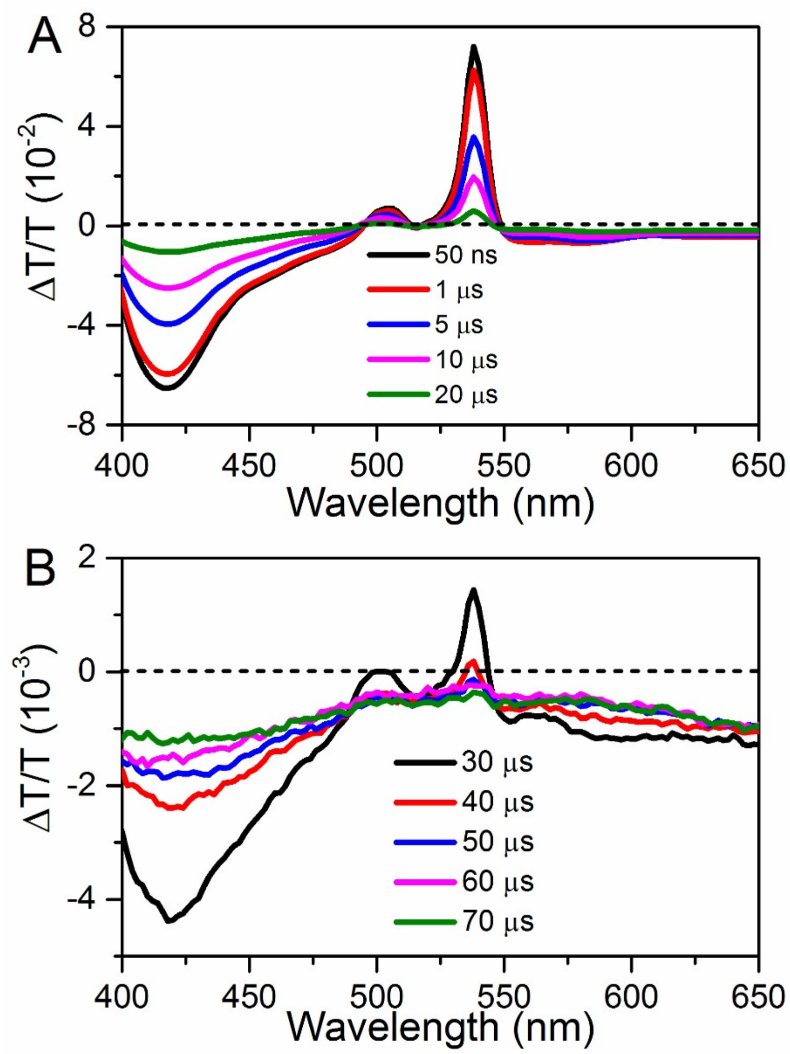

Figure S6. Nanosecond TA measurements of PtOEP doped trimer **4** in THF following excitation of PtOEP at 355 nm at A) short and B) long delays.

7. Fluence independent dynamics of trimer 4

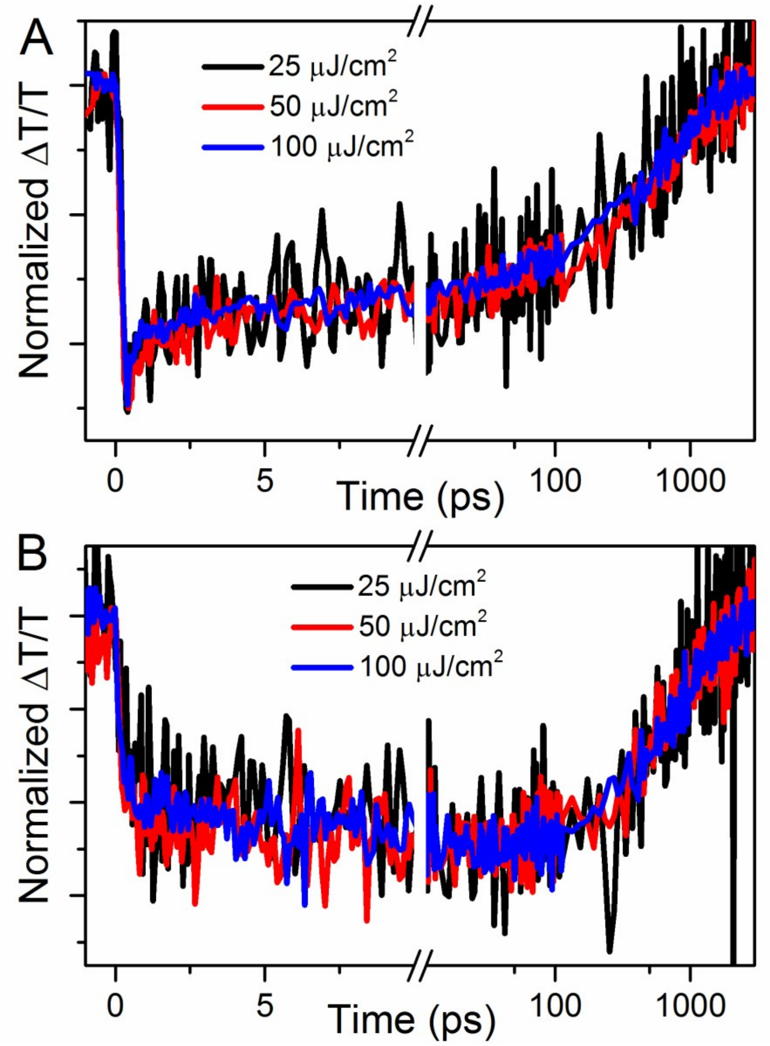

Figure S7. Comparison of normalized dynamics of the absorption at 410 nm (A) and 626 nm (B) of trimer **4**, excited with 500 nm pump with varying pump fluence in degassed THF.

8. The comparison of the TA spectra obtained from iSF and sensitization experiment in dimer 3

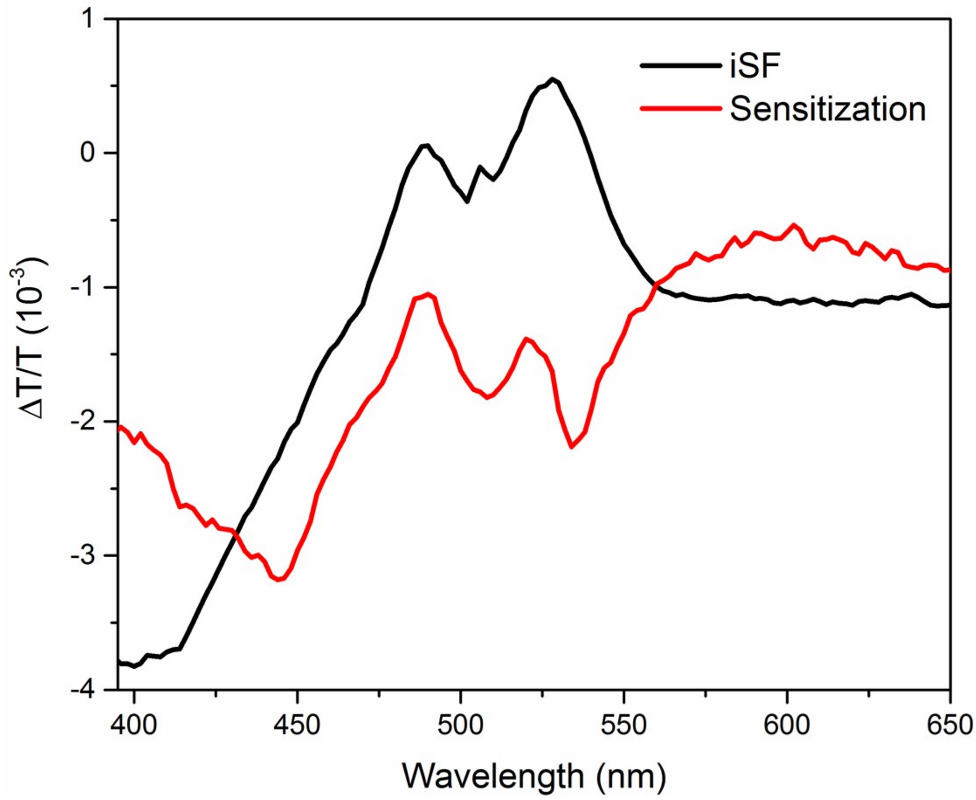

Figure S8. The comparison of the TA spectra obtained from iSF and sensitization experiment in dimer **3**.

9. Solvent independent dynamics of trimer 4

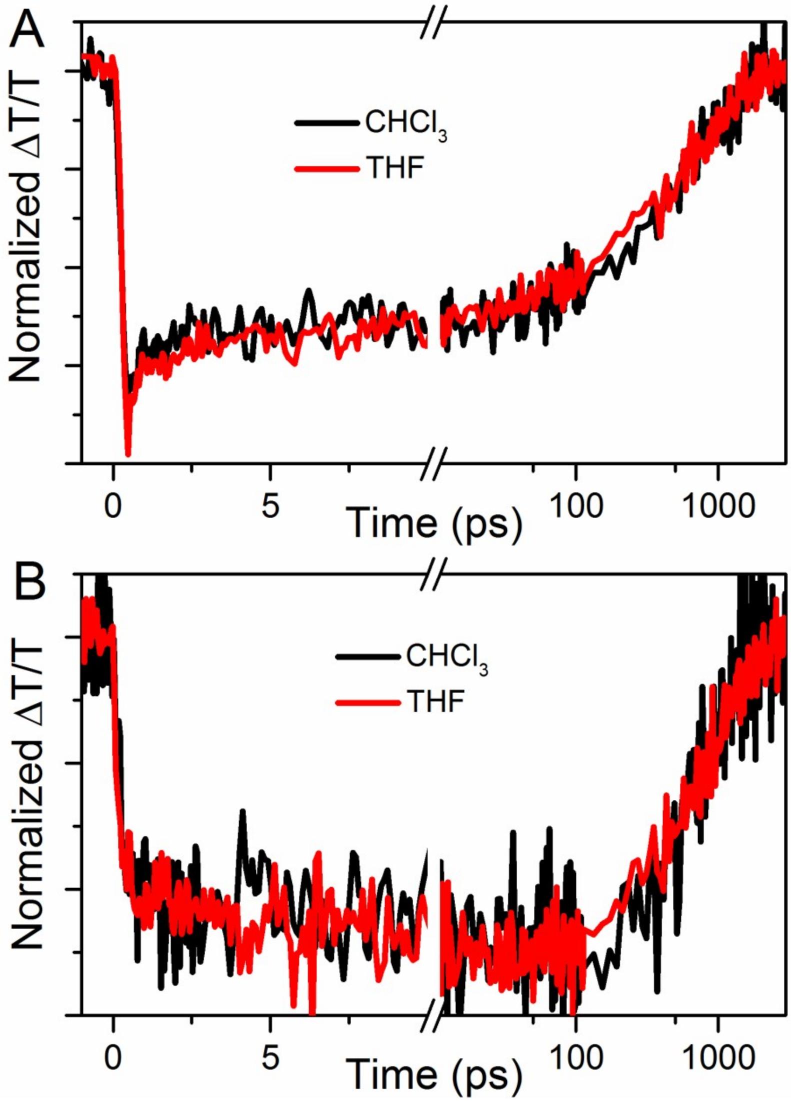

Figure S9. Comparison of normalized dynamics of the absorption at 410 nm (A) and 626 nm (B) of trimer **4** in different solvents.

10. The comparison of the single wavelength dynamics between dimer 3 and trimer 4

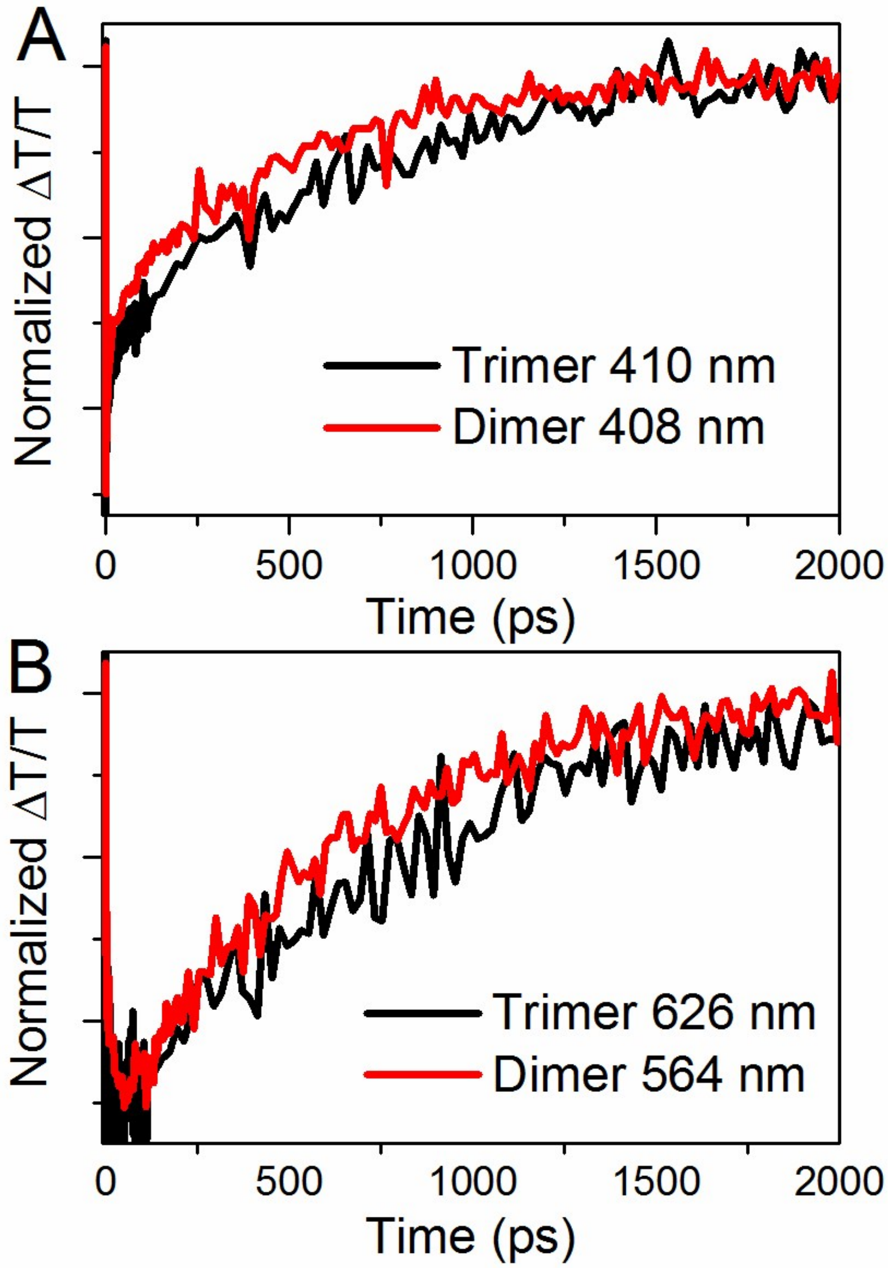

Figure S10. The comparison of the single wavelength dynamics between dimer **3** and trimer **4**.

11. Singlet Fission yield determination

The determination of the yield of triplet involves triplet sensitization experiments using a solution consisting of PtOEP and trimer **4** excited at 355 nm. Triplets are generated in PtOEP by intersystem crossing and are then transferred to trimer **4** via collisional energy transfer.

In the ns-TA experiment of trimer **4** (1.5×10^{-5} M) and PtOEP (2×10^{-5} M), the GSB signal at 2 ns at ~ 538 nm is about -0.0725. The triplet concentration of PtOEP after photoexcitation can be calculated as:

$$c_T^{PtOEP} = \frac{\Delta A_{538\,nm,\ 2\,ns}}{\varepsilon_{538\,nm}^{PtOEP} b} = \frac{-\log_{10}(^{\Delta T}/_{T}+1)}{\varepsilon_{538\,nm}^{PtOEP} b} = \frac{-\log_{10}(-0.0725 -}{51400\,mol^{-1}\,L\,cm^{-1} \times} \times 10^{-6}\,mol\,L^{-1}$$

Triplet energy transfer efficient (□):

$$\Phi_{ET} = \frac{1/10.2\mu s}{1/10.2\mu s + 1/35\mu s} = 77\%$$

In the ns-TA experiment of trimer **4** and PtOEP, the ESA signal at 40 µs at ~ 424 nm is about -0.002389. The molar extinction coefficients of triplet absorption at 424 nm for trimer **4**:

$$\varepsilon_{424\,nm}^{trimer} = \frac{\Delta A}{b * c_T^{PtOEP}} = \frac{-\log_{10}(^{\Delta T}/_{T}+1)}{b * c_T^{PtOEP}} = \frac{-\log_{10}(-0.002389}{0.2\,cm \times 3.18 \times 10^{-6}\,mol} = 2.12 \times 10^{3}\,mol^{-1}\,L\,cm^{-1}$$

In the fs-TA experiment of trimer **4** (8.25×10^{-5} M), the ESA signal at 100 ps at ~ 424 nm is about -0.00241. Using the calculated $\varepsilon_{424\,nm}^{trimer}$ from the sensitization experiment, the triplet concentration from iSF can be calculated as:

$$c_T = \frac{\Delta A_{424\,nm}}{\varepsilon_{424\,nm}^{PtOEP} b} = \frac{-\,log_{10}(^{\Delta T}/_{T} + 1)}{2120\ mol^{-1}\ L\ cm^{-1} \times 0.2\ cm} = 2.47 \times 10^{-6}\ mol\ L^{-1}$$

The total number of photons per pump pulse (500 nm):

$$\frac{photons}{pulse} = \frac{power}{(rep\ rate)(energy\ per\ photon)} = \frac{100 \times 10^{-6} W}{1000\ s^{-1}(3.98 \times 10^{-19} J} = 2.5 \times 10^{11}\ pulse^{-1}$$

Spot volume (V):

$$V = Area\ d = \pi(150 \times 10^{-4} cm)^2 \times 0.2\ cm \times 0.001\ L\ cm^{-3} = 1.41 \times 10^{-7}\ L$$

The fraction of light intensity transmitted ($^{I}/_{I_0}$) of trimer **4** at 500 nm can be calculated as:

$$^{I}/_{I_0} = 10^{-\varepsilon_{500\,nm} c_{trimer} L} = 10^{-2.88 \times 10^4\ cm^{-1}\ mol^{-1}\ L \times 8.25 \times 10^{-}}$$

The initial concentration of singlet state (c_s):

$$c_s = \frac{(photons/pulse)(1 - {}^{I}/_{I_0})}{N_A V} = \frac{(2.5 \times 10^{11}) \times (1 - 0.335)}{(6.02 \times 10^{23}\ mol^{-1})(1.41 \times 10} \ mol\ L^{-1}$$

Triplet yield of trimer 4 (□$_{triplet}$):

$$□_{triplet} = \frac{c_T}{c_s} = \frac{2.47 \times 10^{-6} mol\ L^{-1}}{1.96 \times 10^{-6} mol\ L^{-1}} = 126\%$$

Propagated error in triplet yield determination:[S2]

First, we compute the error in determining the concentration of triplet exciton for PtOEP (c_T^{PtOEP}),

$$\frac{\delta\left(c_T^{PtOEP}\right)}{c_T^{PtOEP}} = \sqrt{\left(\frac{\delta\left(\Delta A_{538\,nm}\right)}{\Delta A_{538\,nm}}\right)^2 + \left(\frac{\delta\left(\varepsilon_{538\,nm}^{PtOEP}\right)}{\varepsilon_{538\,nm}^{PtOEP}}\right)^2}$$

$$= \sqrt{0.05^2 + 0.07^2} = 0.086$$

The propagated error of the molar extinction coefficients of triplet absorption at 424 nm for trimer **4**:

$$\frac{\delta\left(\varepsilon_{424\,nm}^{trimer}\right)}{\varepsilon_{424\,nm}^{trimer}} = \sqrt{\left(\frac{\delta(\Delta A)}{\Delta A}\right)^2 + \left(\frac{\delta\left(c_T^{PtOEP}\right)}{c_T^{PtOEP}}\right)^2}$$

$$= \sqrt{0.05^2 + 0.086^2} = 0.099$$

The propagated error of the triplet concentration from iSF:

$$\frac{\delta\left(c_T\right)}{c_T} = \sqrt{\left(\frac{\delta\left(\Delta A_{424\,nm}\right)}{\Delta A_{424\,nm}}\right)^2 + \left(\frac{\delta\left(\varepsilon_{424\,nm}^{PtOEP}\right)}{\varepsilon_{424\,nm}^{PtOEP}}\right)^2}$$

$$= \sqrt{0.05^2 + 0.099^2} = 0.11$$

The error of photons per pump pulse:

$$\frac{\delta\left(\frac{photons}{pulse}\right)}{\frac{photons}{pulse}} = \frac{\delta(power)}{power}$$

$$= 0.03$$

The error of spot volume:

$$\frac{\delta(V)}{V} = \sqrt{2\left(\frac{\delta(r)}{r}\right)^2}$$

$$= \sqrt{0.08^2 \times 2} = 0.11$$

The propagated error of the fraction of light intensity absorbed (I/I_0) of trimer **4** at 500 nm:

$$\frac{\delta\left(I/I_0\right)}{I/I_0} = \varepsilon_{500\,nm} c_{trimer} L ln(10) \sqrt{\left(\frac{\delta\left(\varepsilon_{500\,nm}\right)}{\varepsilon_{500\,nm}}\right)^2 + \left(\frac{\delta\left(c_{trimer}\right)}{c_{trimer}}\right)^2}$$

$$= 0.474 \times 2.30 \times \sqrt{0.07^2 + 0.02^2} = 0.079$$

The propagated error of the initial concentration of singlet state (c_s):

$$\frac{\delta(c_s)}{c_s} = \sqrt{\left(\frac{\delta\left(\frac{photons}{pulse}\right)}{\frac{photons}{pulse}}\right)^2 + \left(\frac{\delta(I/I_0)}{I/I_0}\right)^2 + \left(\frac{\delta(V)}{V}\right)^2}$$

$$= \sqrt{0.03^2 + 0.079^2 + 0.11^2} = 0.138$$

The propagated error of triplet yield of trimer 4 ($\square_{\text{triplet}}$):

$$\frac{\delta(\square_{triplet})}{\square_{triplet}} = \sqrt{\left(\frac{\delta(c_s)}{c_s}\right)^2 + \left(\frac{\delta(c_T)}{c_T}\right)^2}$$

$$= \sqrt{0.138^2 + 0.11^2} = 0.17$$

12. Copies of the ^{1}H NMR spectra and MALDI-TOF spectra of new compounds

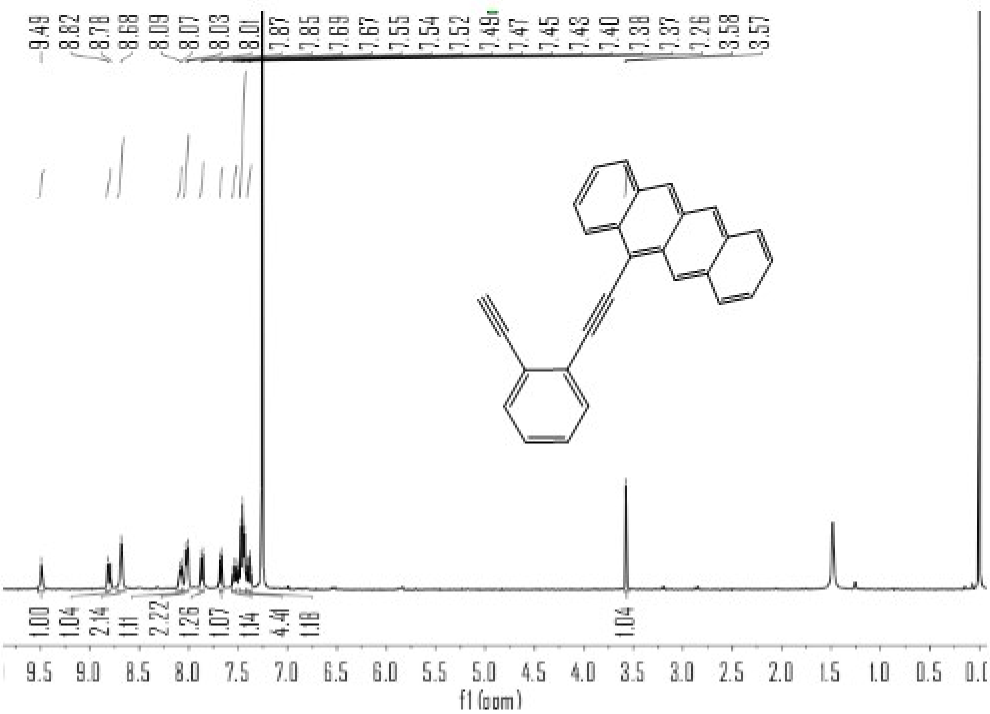

Figure S11. The ^{1}H NMR spectrum of monomer **1**.

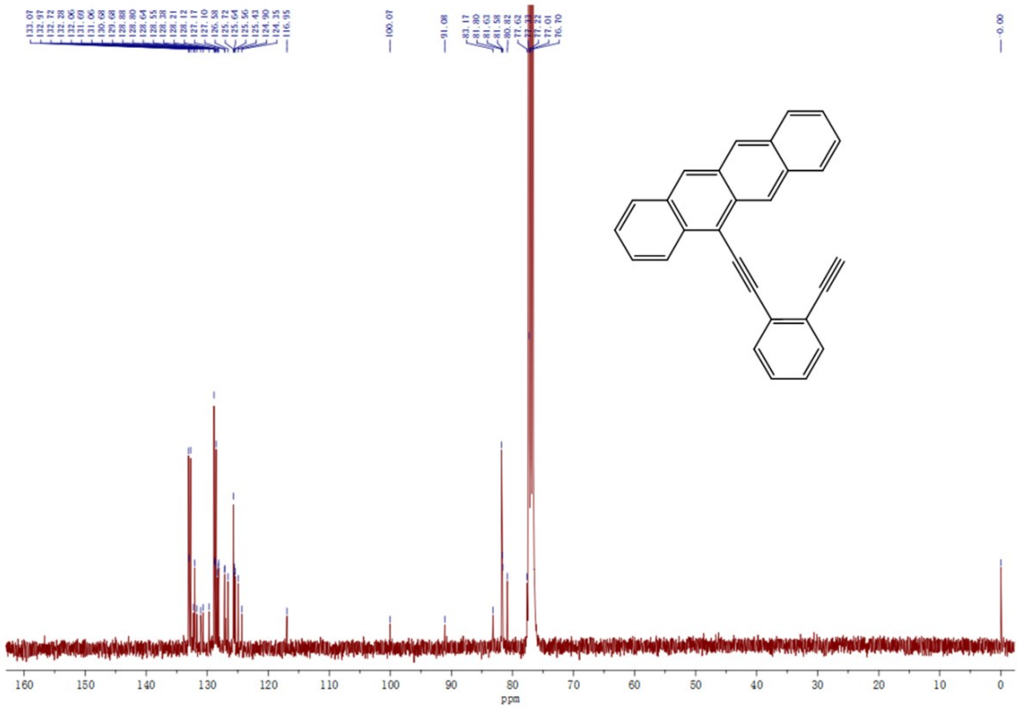

Figure S12. The ^{13}C NMR spectrum of monomer **1**.

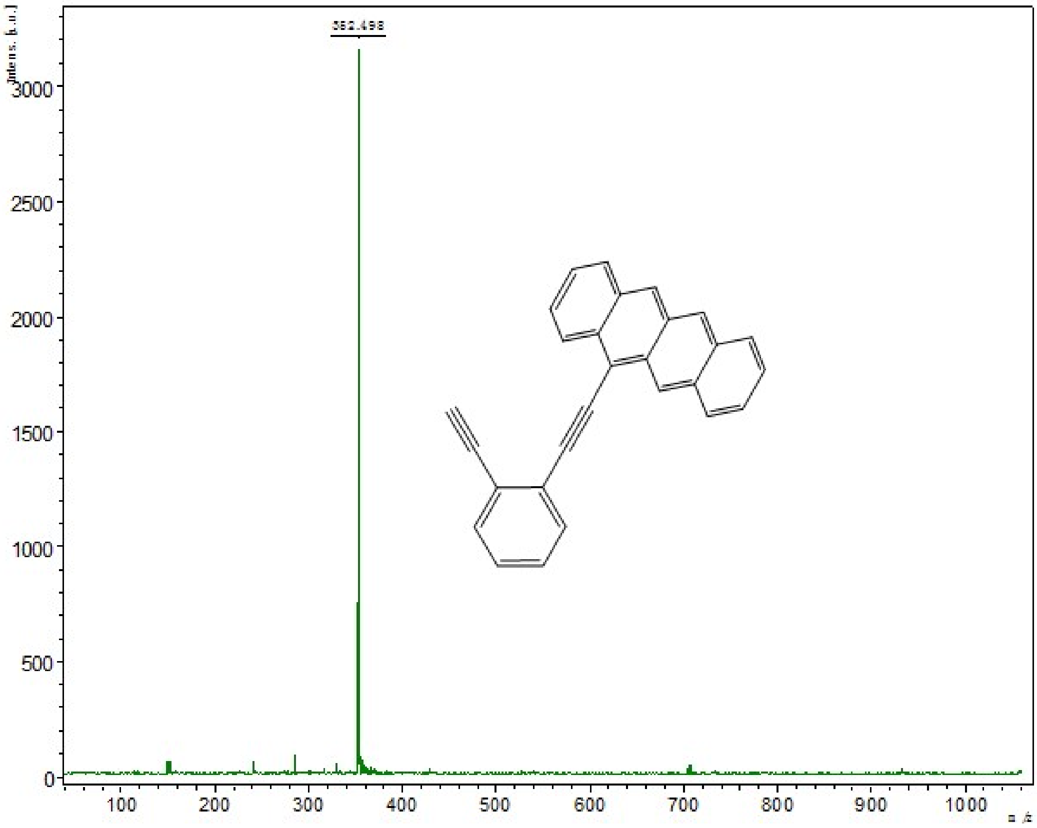

Figure S13. The MALDI-TOF spectrum of monomer **1**.

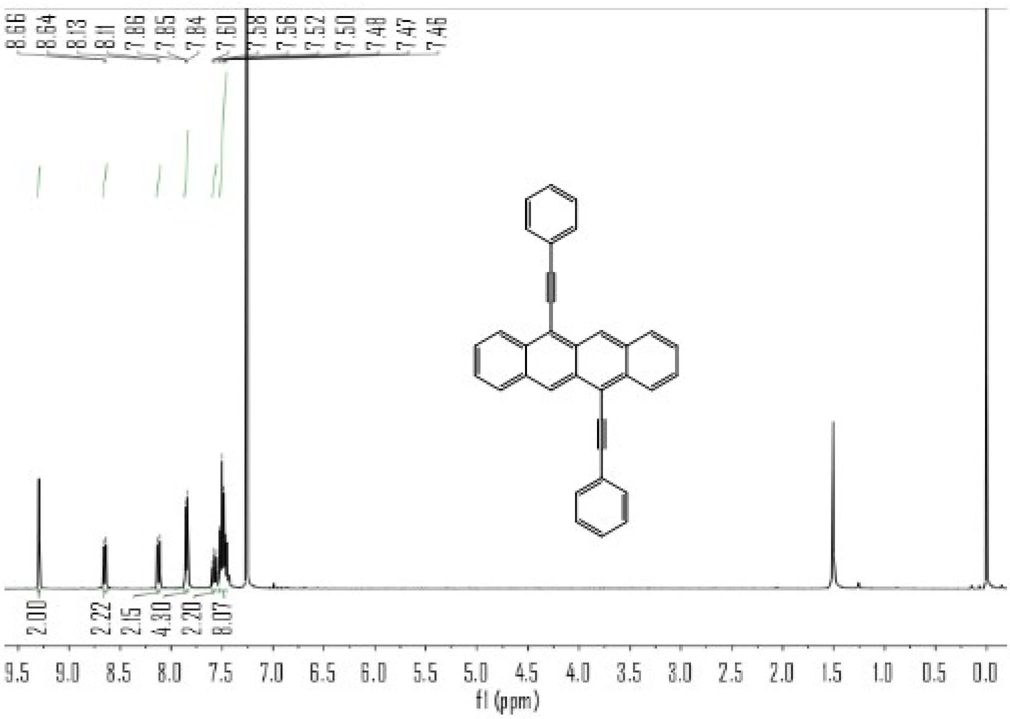

Figure S14. The ^{1}H NMR spectrum of monomer **2**.

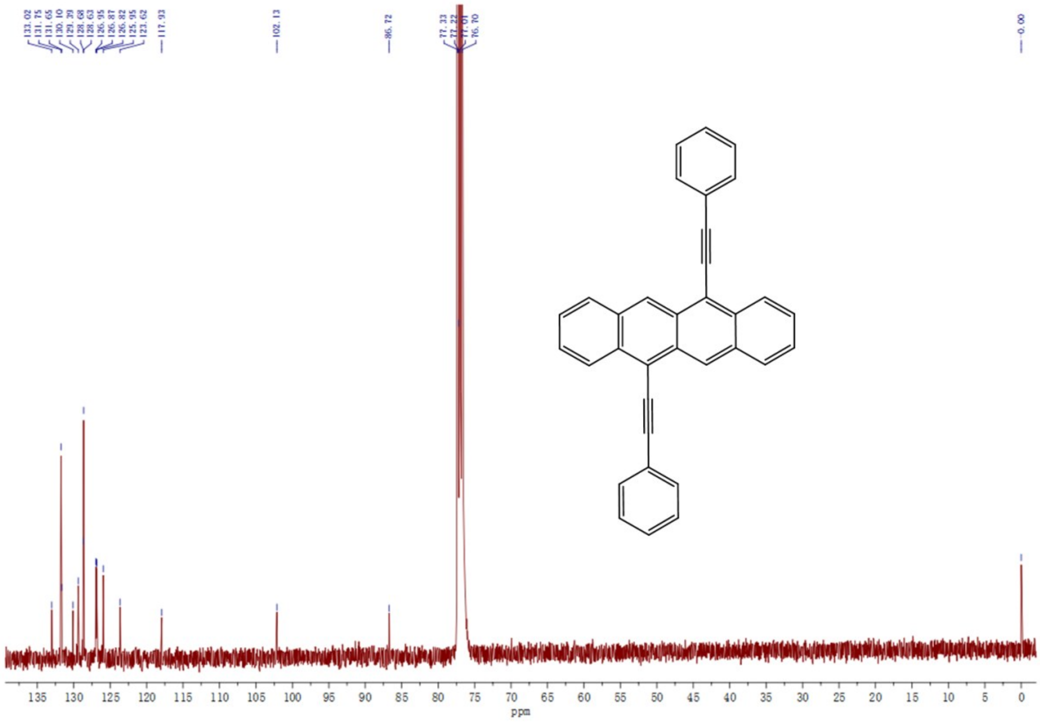

Figure S15. The ^{13}C NMR spectrum of monomer **2**.

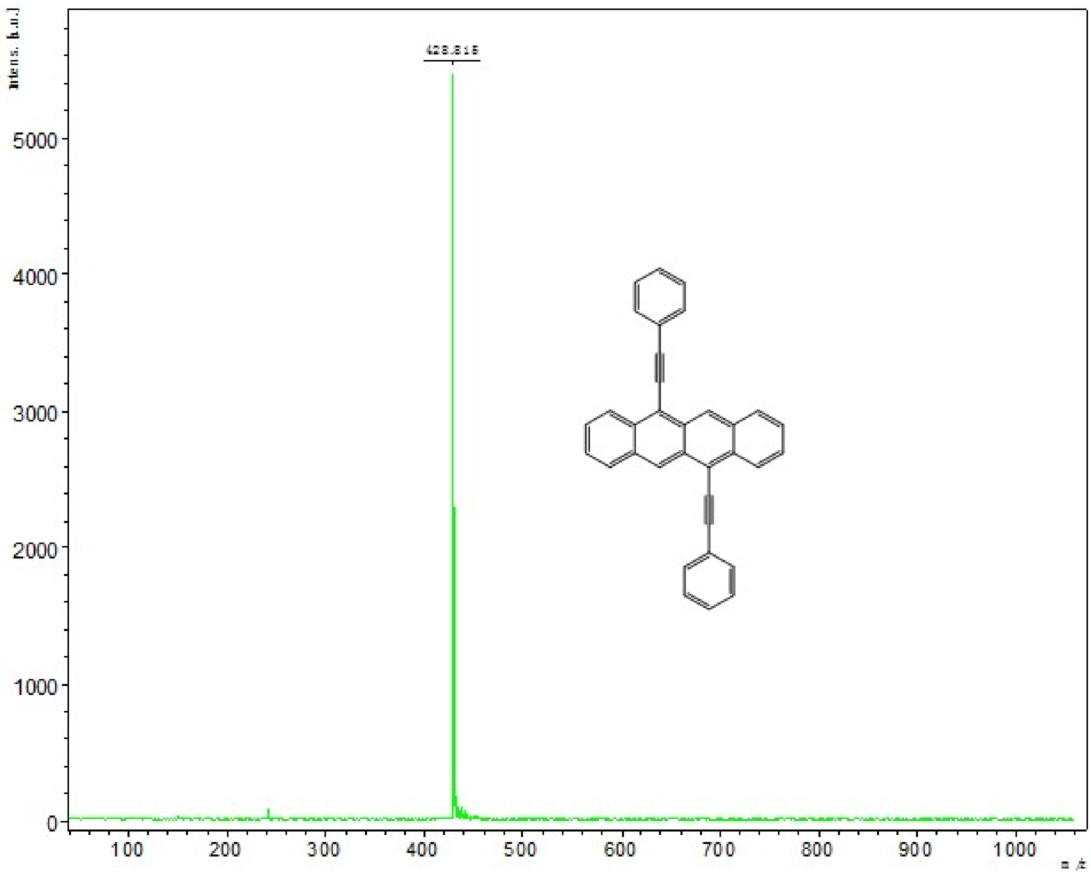

Figure S16. The MALDI-TOF spectrum of monomer **2**.

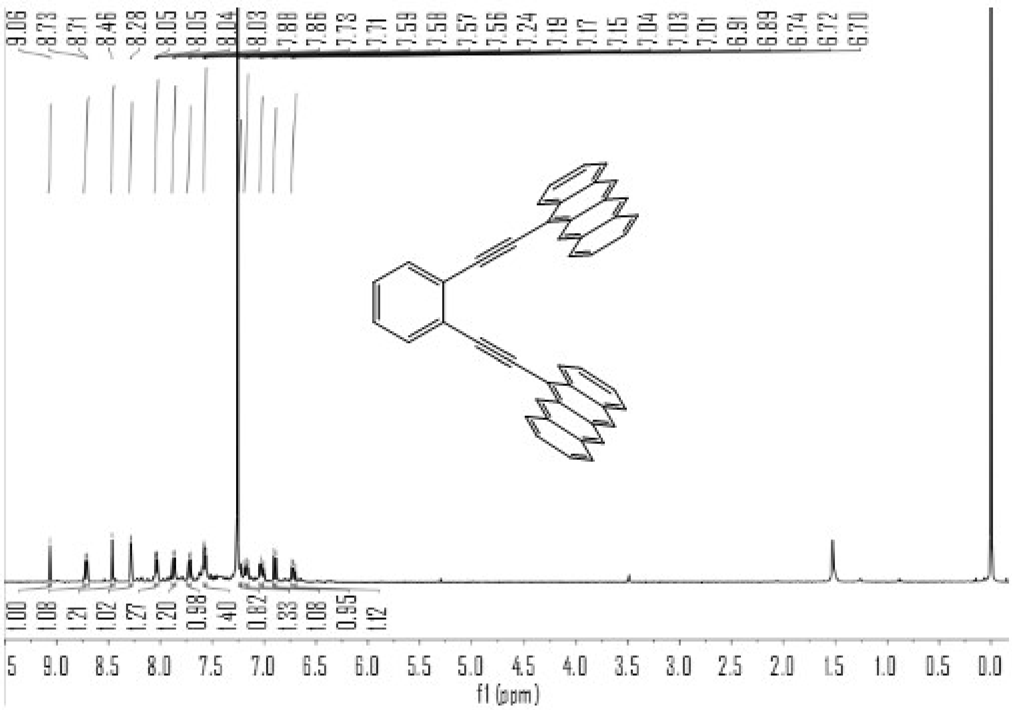

Figure S17. The [1]H NMR spectrum of dimer **3**.

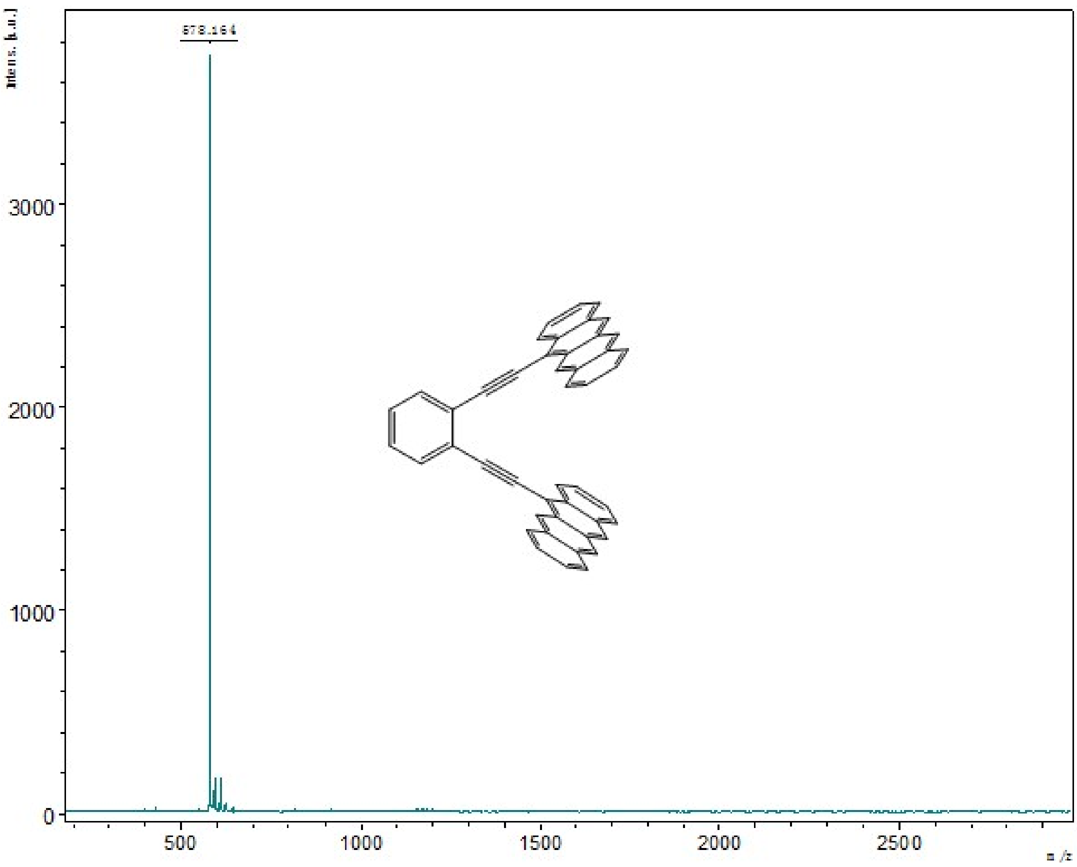

Figure S18. The MALDI-TOF spectrum of dimer **3**.

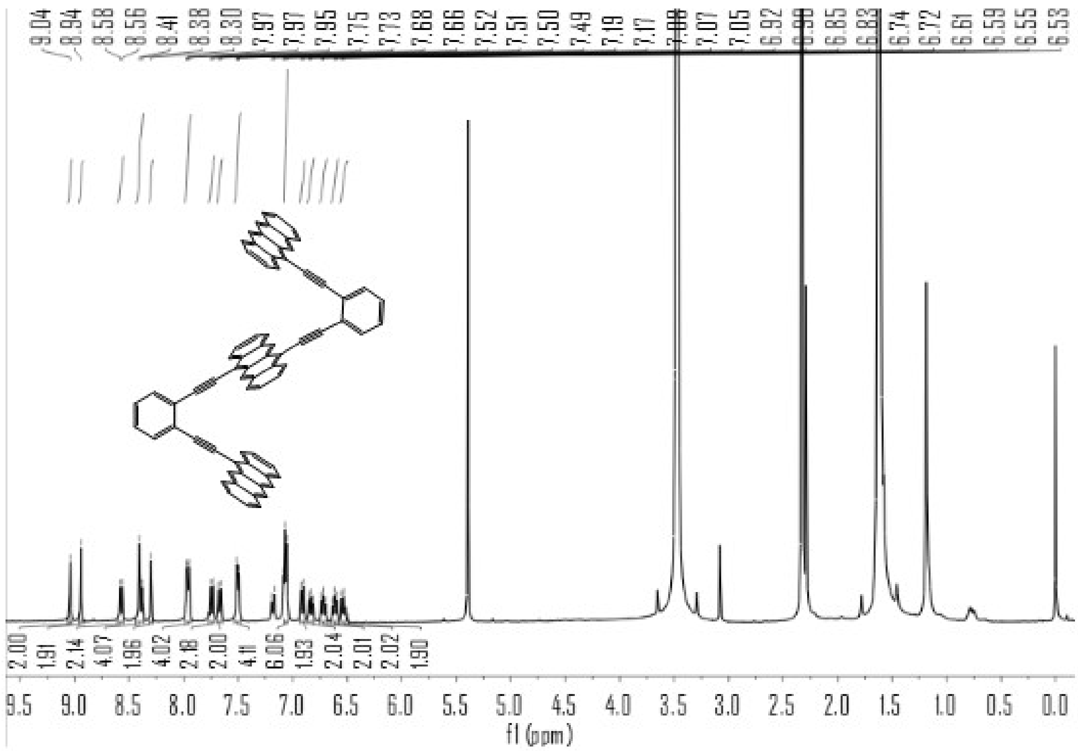

Figure S19. The ^{1}H NMR spectrum of trimer **4**.

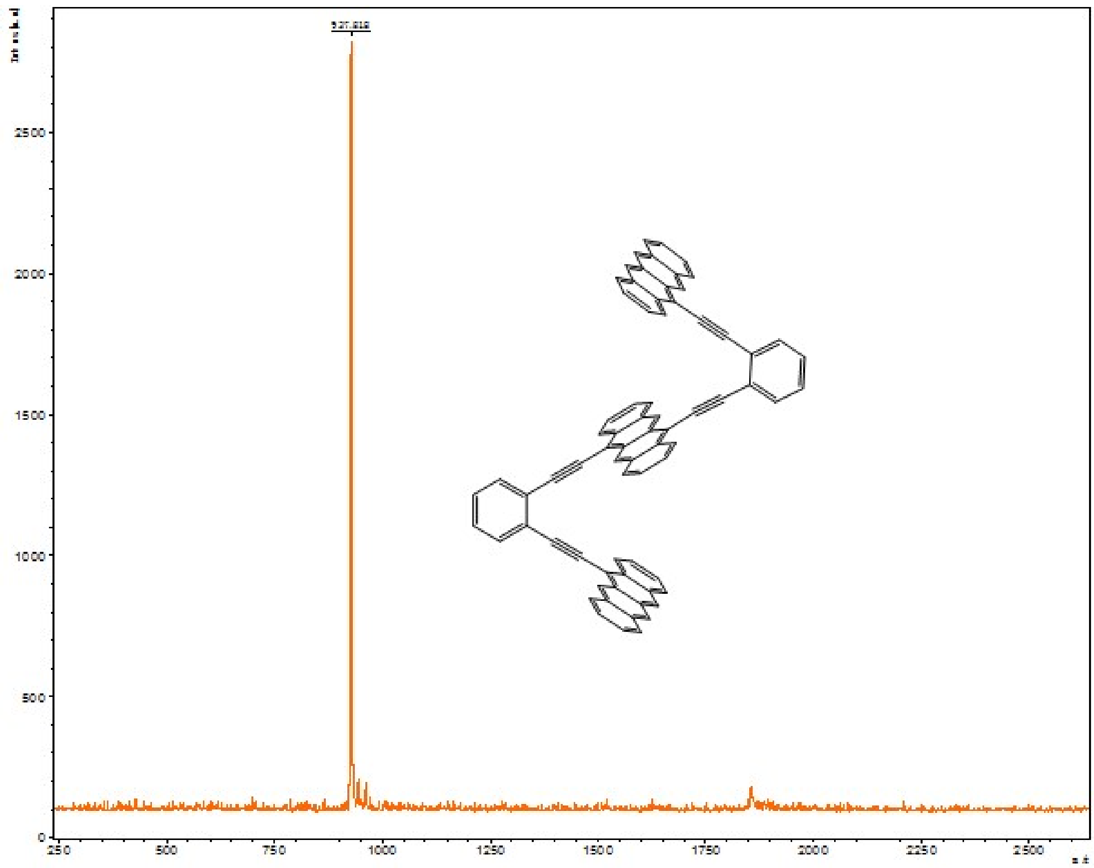

Figure S20. The MALDI-TOF spectrum of trimer **4**.

References

S1 N. V. Korovina, S. Das, Z. Nett, X. Feng, J. Joy, R. Haiges, A. I. Krylov, S. E. Bradforth and M. E. Thompson, *J. Am. Chem. Soc.*, 2016, **138**, 617-627.

S2 B. J. Walker, A. J. Musser, D. Beljonne and R. H. Friend, *Nat. Chem.*, 2013, **5**, 1019-1024.

Appendix. Geometry optimization of S_0 states

Dimer 3

C	-0.67186	6.614	0.18678
H	-1.19665	7.55276	0.33369
C	-1.33992	5.4131	0.37673
H	-2.38321	5.40422	0.67543
C	-0.68065	4.1901	0.19601
C	-1.36645	2.95914	0.41531
C	-1.92646	1.90194	0.61473
C	-2.50975	0.61564	0.79811
C	-3.86802	0.40113	0.51197
C	-4.73783	1.45976	0.09625
H	-4.32665	2.46068	0.00993
C	-6.0483	1.22033	-0.18439
H	-6.69381	2.03589	-0.49652
C	-6.5904	-0.09654	-0.07303
H	-7.63941	-0.26367	-0.29771
C	-5.79625	-1.1317	0.3112
H	-6.19845	-2.13796	0.39674
C	-4.40921	-0.92748	0.61198
C	-3.5773	-1.98488	0.95072
H	-3.98345	-2.99356	0.97876
C	-2.21502	-1.79391	1.23423
C	-1.35712	-2.87893	1.49769
H	-1.76545	-3.88642	1.47004
C	-0.00908	-2.69179	1.75687
C	0.89508	-3.78728	1.95612
H	0.50034	-4.79878	1.90242
C	2.21523	-3.56638	2.19982

H	2.89173	-4.40426	2.34201
C	2.72932	-2.23403	2.27681
H	3.78694	-2.07963	2.46709
C	1.90664	-1.16623	2.09396
H	2.29634	-0.15299	2.13239
C	0.5158	-1.35216	1.8059
C	-0.31661	-0.27846	1.52376
H	0.10015	0.72436	1.51072
C	-1.67127	-0.46289	1.20537
C	0.6718	6.614	-0.18674
H	1.19659	7.55276	-0.33365
C	1.33986	5.41309	-0.37666
H	2.38316	5.40421	-0.67534
C	0.68059	4.19009	-0.19593
C	1.36644	2.95915	-0.41515
C	1.92655	1.90201	-0.61458
C	2.50979	0.61571	-0.7981
C	3.86809	0.40117	-0.51208
C	4.73793	1.45975	-0.09632
H	4.32676	2.46067	-0.00988
C	6.04841	1.2203	0.18423
H	6.69394	2.03583	0.49638
C	6.5905	-0.09656	0.07271
H	7.63952	-0.26372	0.29732
C	5.79633	-1.13168	-0.31158
H	6.19852	-2.13794	-0.39722
C	4.40928	-0.92743	-0.61226
C	3.57735	-1.98481	-0.95104
H	3.98352	-2.99347	-0.97928
C	2.21503	-1.79382	-1.23439

C	1.35712	-2.87882	-1.49789
H	1.76548	-3.88631	-1.47049
C	0.00905	-2.69167	-1.75688
C	-0.89511	-3.78715	-1.95623
H	-0.50033	-4.79865	-1.9028
C	-2.21529	-3.56624	-2.19972
H	-2.89179	-4.40413	-2.34197
C	-2.72944	-2.2339	-2.27639
H	-3.78709	-2.07949	-2.4665
C	-1.90677	-1.16611	-2.09342
H	-2.29651	-0.15287	-2.13164
C	-0.51589	-1.35205	-1.8056
C	0.31655	-0.27837	-1.52347
H	-0.10022	0.72445	-1.5103
C	1.67127	-0.4628	-1.20534

Trimer 4

C	5.43529	3.37404	0.931
H	5.9415	4.30841	1.13881
C	4.24922	3.37722	0.21079
H	3.82138	4.30729	-0.14074
C	3.57531	2.17883	-0.06547
C	2.34218	2.19477	-0.77735
C	1.28018	2.1868	-1.36019
C	5.96985	2.17016	1.39163
H	6.89328	2.16703	1.95728
C	5.32132	0.97326	1.12334
H	5.7328	0.03475	1.47216
C	4.12469	0.95409	0.39138

C	3.47974	-0.28139	0.10296
C	2.92694	-1.32645	-0.16162
C	2.19111	-2.4959	-0.49585
C	2.23882	-3.6341	0.32606
C	3.11177	-3.73144	1.45573
H	3.764	-2.89462	1.67511
C	3.12142	-4.85044	2.23539
H	3.79212	-4.91361	3.08422
C	2.25077	-5.9452	1.95373
H	2.28117	-6.82879	2.57864
C	1.40471	-5.88815	0.8889
H	0.75919	-6.72382	0.64698
C	1.38449	-4.74683	0.02797
C	0.55246	-4.70672	-1.08406
H	-0.08925	-5.55346	-1.29471
C	0.52507	-3.60027	-1.94056
C	-0.3097	-3.57355	-3.09428
C	-0.35746	-2.43534	-3.91617
C	-1.23051	-2.33795	-5.04575
H	-1.88278	-3.17474	-5.2651
C	-1.24025	-1.2189	-5.82534
H	-1.91107	-1.15567	-6.67407
C	-0.36961	-0.12413	-5.54368
H	-0.40011	0.7595	-6.16853
C	0.47654	-0.18123	-4.47893
H	1.12206	0.65444	-4.237
C	0.49687	-1.32261	-3.61808
C	1.32894	-1.36273	-2.50608
H	1.97063	-0.51598	-2.29542
C	1.35637	-2.46919	-1.64959

C	-1.04559	-4.74297	-3.42845
C	-1.59845	-5.78805	-3.69284
C	-2.24355	-7.02348	-3.9811
C	-1.69426	-8.24826	-3.52422
C	-3.44027	-7.04256	-4.71292
C	-2.36835	-9.44659	-3.80032
C	-4.08897	-8.23941	-4.98106
H	-3.85168	-6.10403	-5.06174
C	-3.55449	-9.44331	-4.5204
H	-1.94056	-10.37669	-3.44881
H	-5.01247	-8.23621	-5.54659
H	-4.06083	-10.37764	-4.72811
C	-0.46107	-8.26432	-2.81247
C	0.60099	-8.25638	-2.22975
C	2.33394	-6.11325	-2.92483
C	3.05694	-4.95073	-3.15161
C	2.65571	-6.98373	-1.87249
C	2.69989	-4.03943	-4.19712
C	4.1365	-4.60044	-2.26431
C	3.79833	-6.68743	-1.04918
C	1.83913	-8.10575	-1.54469
H	1.88733	-4.3088	-4.86076
C	3.33324	-2.84158	-4.32074
C	4.77263	-3.32413	-2.43083
C	4.49668	-5.48189	-1.25746
C	4.14168	-7.56854	-0.0114
C	2.19899	-8.97307	-0.49988
H	3.02938	-2.14269	-5.08966
C	4.38116	-2.47573	-3.4188
H	5.55715	-3.04469	-1.73688

H	5.31249	-5.22902	-0.58907
H	5.00028	-7.33662	0.60984
C	3.3902	-8.70333	0.26186
C	1.39924	-10.10608	-0.13721
H	4.85043	-1.50506	-3.52186
C	3.7329	-9.5874	1.33969
C	1.7611	-10.91634	0.89548
H	0.4996	-10.30139	-0.70833
H	4.63514	-9.37926	1.90426
C	2.94876	-10.65526	1.64746
H	1.14849	-11.77067	1.15665
H	3.21559	-11.31655	2.4627
H	1.48318	-6.33915	-3.55641
C	0.04206	2.0362	-2.04525
C	-0.31779	2.90359	-3.09
C	-0.7745	0.91413	-1.71756
C	-1.50897	2.63389	-3.85179
C	0.48197	4.03663	-3.45257
C	-1.91709	0.61788	-2.54093
C	-0.45276	0.04357	-0.66528
C	-1.85163	3.51803	-4.92959
C	-2.26043	1.49906	-3.57865
C	0.12015	4.84694	-4.48523
H	1.38158	4.23192	-2.8814
C	-2.61543	-0.58769	-2.33278
C	-1.17576	-1.11897	-0.4386
H	0.39798	0.26942	-0.03365
C	-1.06748	4.58591	-5.23727
H	-2.75382	3.30989	-5.49424
H	-3.11902	1.26718	-4.19991

H	0.73276	5.7013	-4.74632
C	-2.25528	-1.46921	-1.32597
H	-3.43124	-0.8405	-3.00118
C	-0.81876	-2.03034	0.60686
H	-1.33427	5.24722	-6.0525
C	-2.89139	-2.74554	-1.15957
C	-1.45207	-3.22821	0.73035
H	-0.00626	-1.76097	1.2706
C	-2.49992	-3.59403	-0.17168
H	-3.67589	-3.02493	-1.85357
H	-1.14821	-3.92717	1.49922
H	-2.96916	-4.56473	-0.06874