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Self-association of oligothiophenes in isotropic systems

(Supplementary Information)

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Section S1. ^{1}H NMR dilution experiments

A) Thiophene

Table S1. ^{1}H NMR results for the dissolution studies of thiophene in $CDCl_3$.

NMR tube	[sample] / mol·dm^{-3}	δ(H1) / ppm	δ(H2) / ppm
1	1.4298	7.3143	7.1029
	1.1915	7.3188	7.1059
	1.0213	7.3251	7.1108
	0.8936	7.3291	7.1142
	0.7149	7.3357	7.1185
	0.6499	7.3371	7.1197
	0.5106	7.3426	7.1241
2	0.9386	7.3259	7.1114
	0.7822	7.3315	7.1156
	0.5866	7.3383	7.1203
3	0.4365	7.3430	7.1243
	0.3274	7.3473	7.1274
	0.2619	7.3496	7.1296

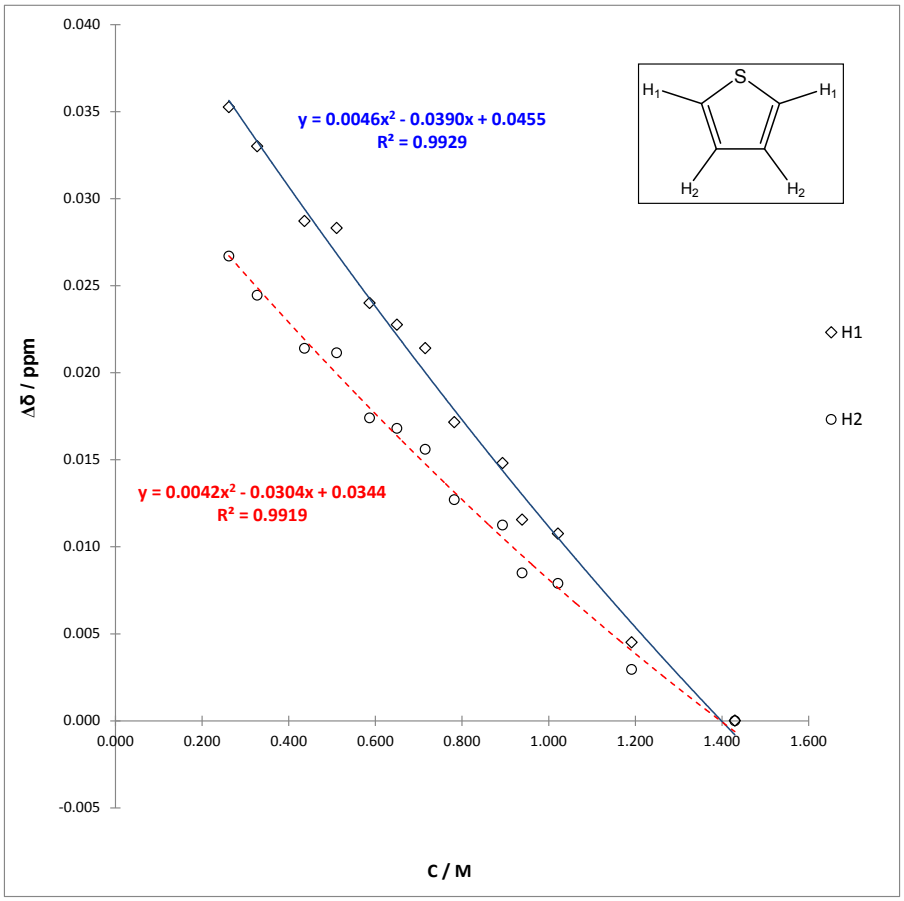

Figure S1. Plot of $\Delta\delta = f$ (sample concentration) for the NMR dissolution studies of thiophene in $CDCl_3$.

Table S2. Results derived from the least squares fitting of equation 2 (in the manuscript) for the NMR dissolution studies of thiophene in $CDCl_3$.

Proton	K_{eq}	$\Sigma(\delta_{calc} - \delta_{exp})^2$
H1	0.059	$1.0 \cdot 10^{-5}$
H2	0.077	$6.7 \cdot 10^{-6}$

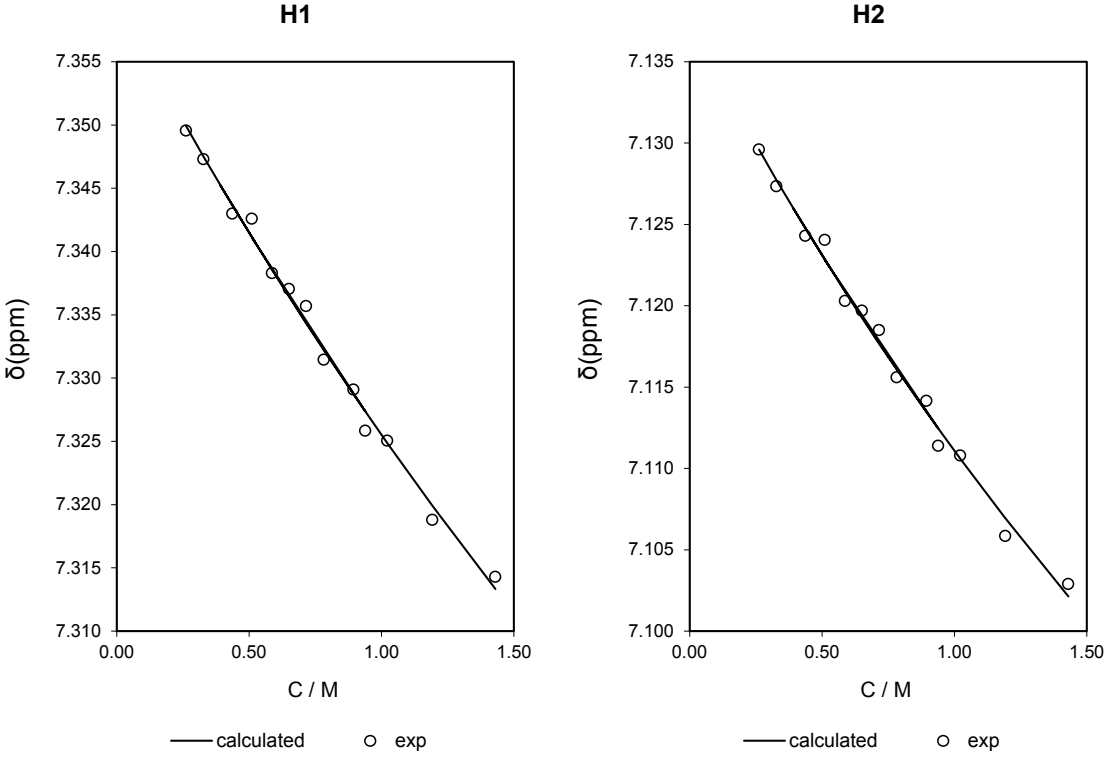

Figure S2. Graphical representation of the fitting results of the calculated chemical shifts, δ, to the experimental data for the NMR dissolution studies of thiophene in $CDCl_3$.

Table S3. ^{1}H NMR results for the dissolution studies of thiophene in acetone-d_6.

NMR tube	[sample] / mol·dm^{-3}	δ(H1) / ppm
1	1.1392	7.4939
	0.9493	7.4952
	0.8137	7.4965
	0.7120	7.4969
	0.5696	7.4984
	0.5178	7.4993
	0.4068	7.5007
2	0.7643	7.4969
	0.6369	7.4981
	0.2548	7.5013
3	0.4660	7.4994
	0.1553	7.5031

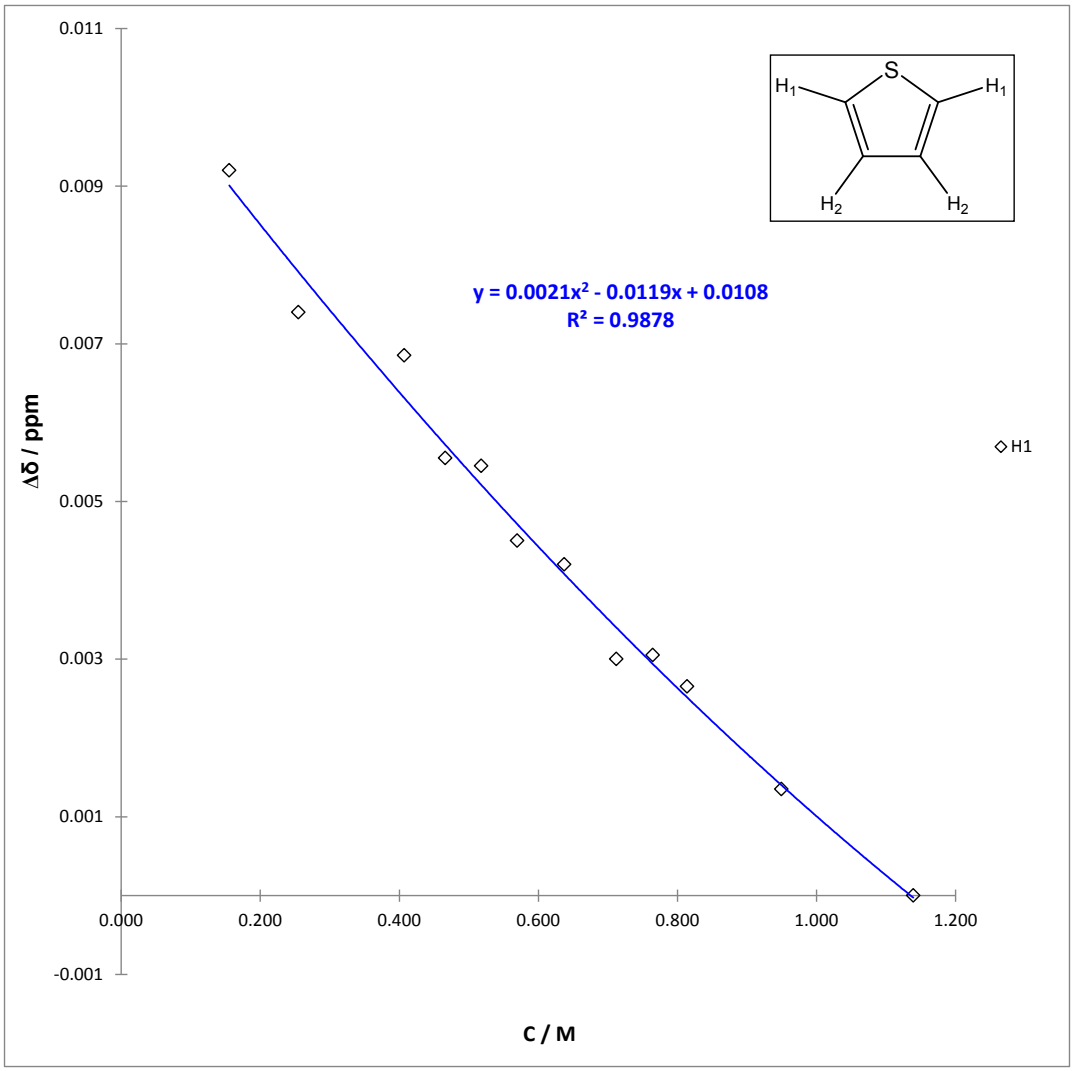

Figure S3. Plot of $\Delta\delta = f$ (sample concentration) for the NMR dissolution studies of thiophene in acetone-d_6.

Table S4. Results derived from the least squares fitting of equation 2 (in the manuscript) for the NMR dissolution studies of thiophene in acetone-d_6.

Proton	K_{eq}	$\Sigma(\delta_{calc} - \delta_{exp})^2$
H1	0.107	$9.3 \cdot 10^{-7}$

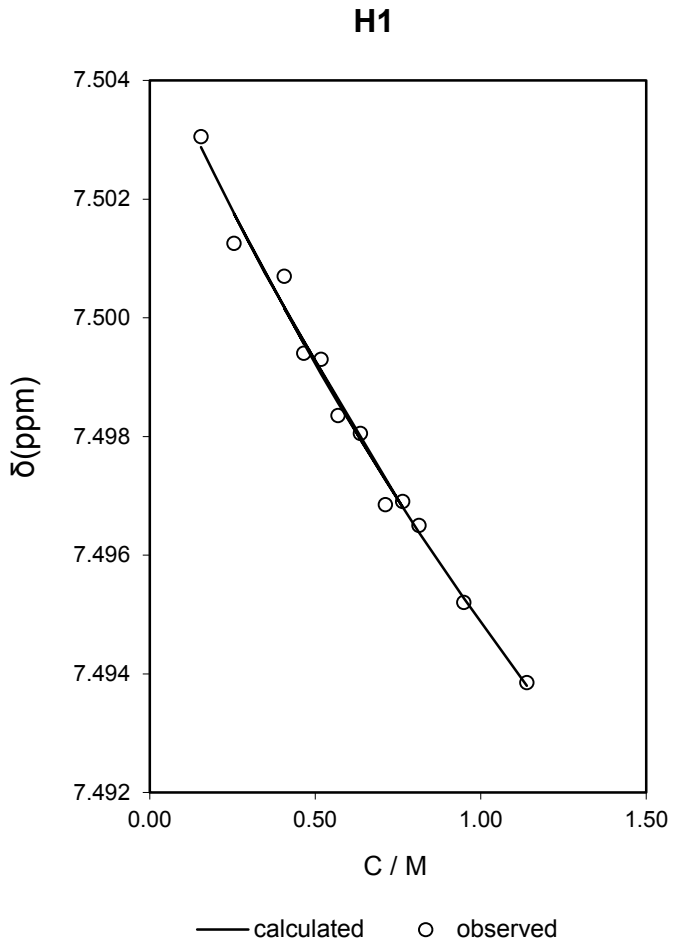

Figure S4. Graphical representation of the fitting results of the calculated chemical shifts, δ, to the experimental data for the NMR dissolution studies of thiophene in acetone-d_6.

B) 2,2'-Bithiophene (22-BT)

Table S5. ^{1}H NMR results for the dissolution studies of 22-BT in $CDCl_3$.

NMR tube	[sample] / mol·dm^{-3}	δ(H1) / ppm	δ(H2) / ppm	δ(H3) / ppm
1	0.6136	6.9830	7.1722	7.1532
	0.5113	6.9880	7.1783	7.1566
	0.3835	6.9949	7.1867	7.1617
	0.2557	7.0025	7.1958	7.1674
	0.2191	7.0045	7.1981	7.1690
2	0.1185	7.0096	7.2042	7.1727
	0.0862	7.0117	7.2067	7.1743
	0.0677	7.0126	7.2076	7.1748
3	0.0657	7.0122	7.2075	7.1746
	0.0411	7.0140	7.2093	7.1759
	0.0299	7.0145	7.2102	7.1763
	0.0219	7.0154	7.2111	7.1770

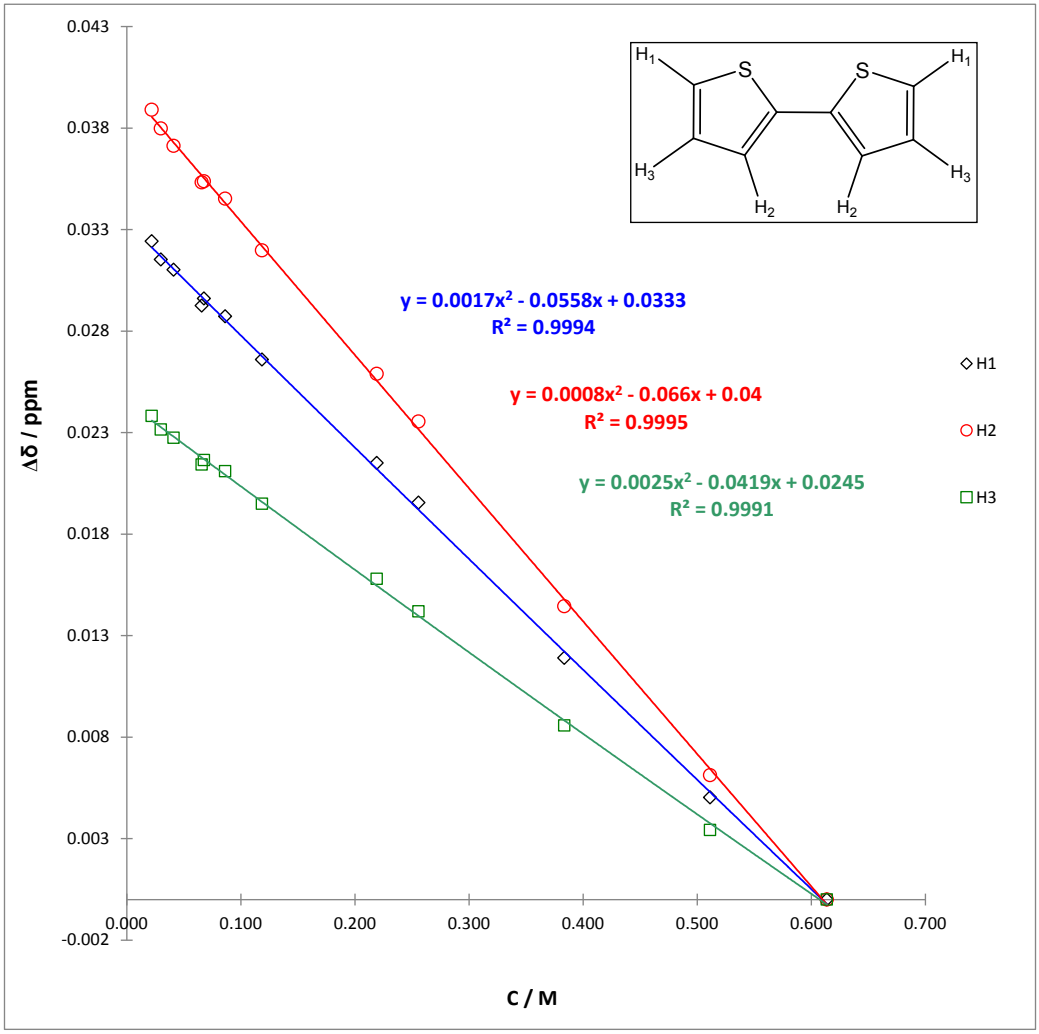

Figure S5. Plot of $\Delta\delta = f$ (sample concentration) for the NMR dissolution studies of 22-BT in $CDCl_3$.

Table S6. Results derived from the least squares fitting of equation 2 (in the manuscript) for the NMR dissolution studies of 22-BT in $CDCl_3$.

Proton	K_{eq}	$\Sigma(\delta_{calc} - \delta_{exp})^2$
H1	0.022	$8.2 \cdot 10^{-7}$
H2	0.020	$9.9 \cdot 10^{-7}$
H3	0.027	$6.4 \cdot 10^{-7}$

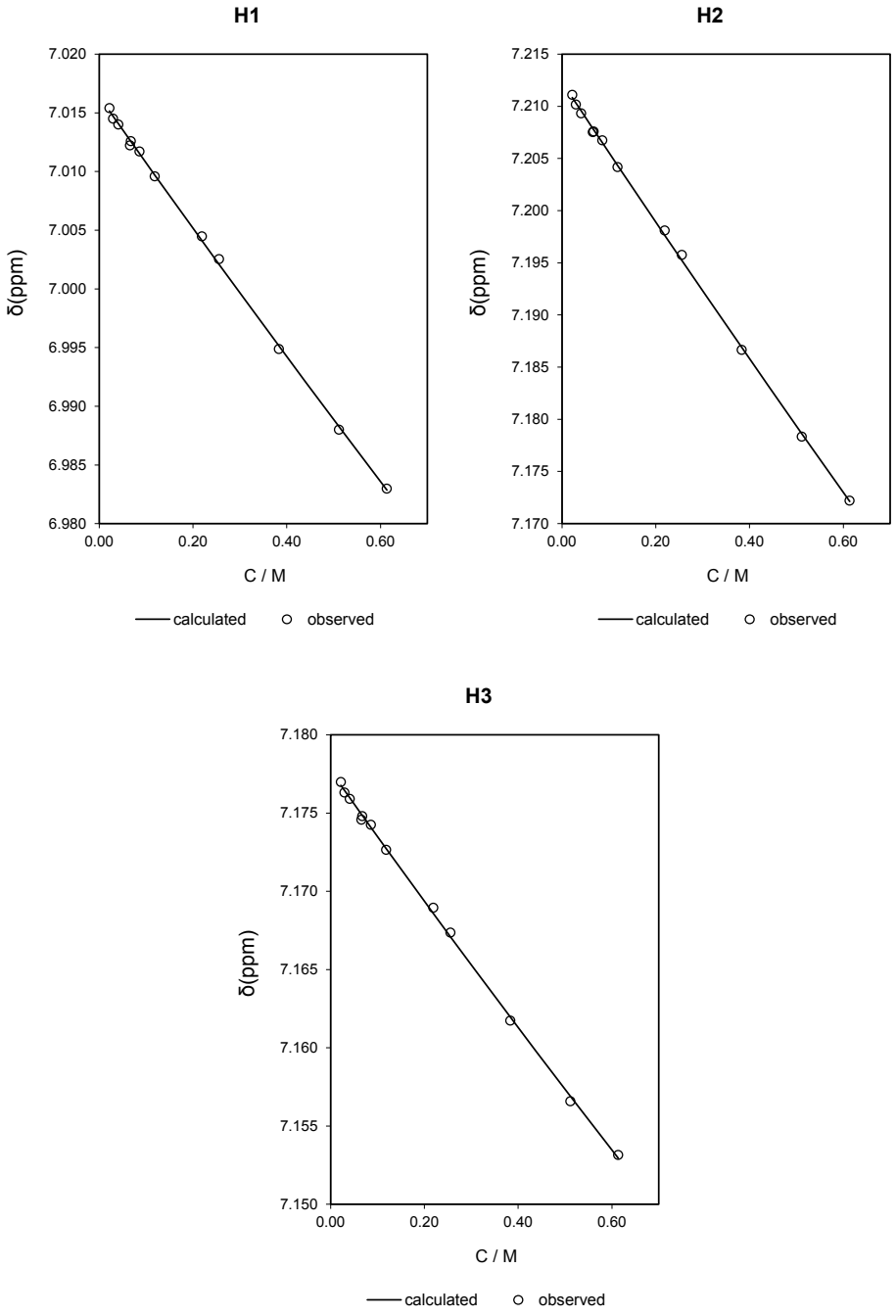

Figure S6. Graphical representation of the fitting results of the calculated chemical shifts, δ, to the experimental data for the NMR dissolution studies of 22-BT in $CDCl_3$.

Table S7. ^{1}H NMR results for the dissolution studies of 22-BT in acetone-d_6.

NMR tube	[sample] / mol·dm^{-3}	δ(H1) / ppm	δ(H2) / ppm
1	0.7970	7.0829	7.4033
	0.6832	7.0843	7.4067
	0.5978	7.0863	7.4104
	0.5313	7.0873	7.4130
	0.4347	7.0885	7.4156
	0.3188	7.0902	7.4191
2	0.2159	7.0923	7.4236
	0.1080	7.0939	7.4268
	0.0864	7.0945	7.4281
3	0.0842	7.0950	7.4289
	0.0561	7.0948	7.4288
	0.0421	7.0955	7.4302
	0.0337	7.0957	7.4305

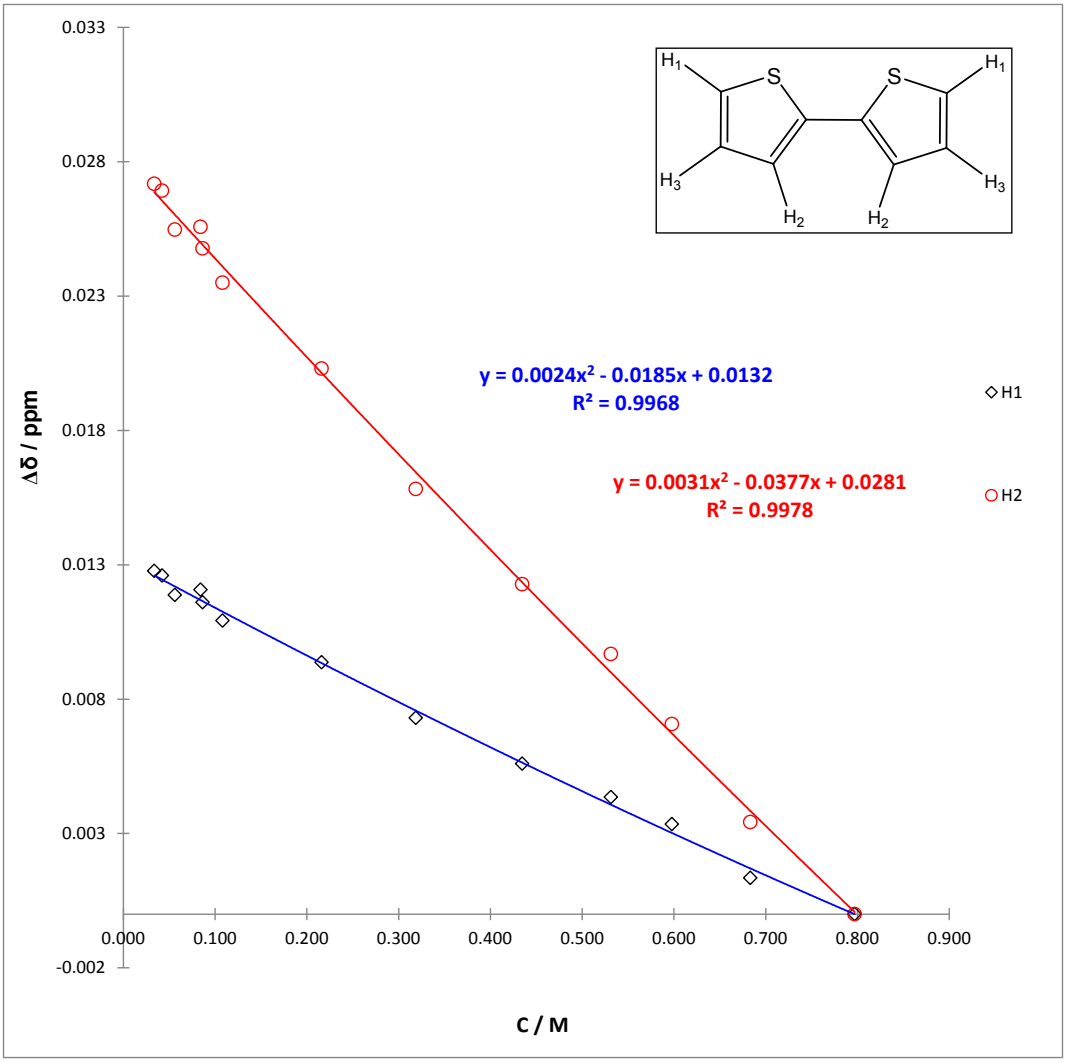

Figure S7. Plot of $\Delta\delta = f$ (sample concentration) for the NMR dissolution studies of 22-BT in acetone-d_6.

Table S8. Results derived from the least squares fitting of equation 2 (in the manuscript) for the NMR dissolution studies of 22-BT in acetone-d_6.

Proton	K_{eq}	$\Sigma(\delta_{calc} - \delta_{exp})^2$
H1	0.057	$7.9 \cdot 10^{-7}$
H2	0.036	$2.4 \cdot 10^{-6}$

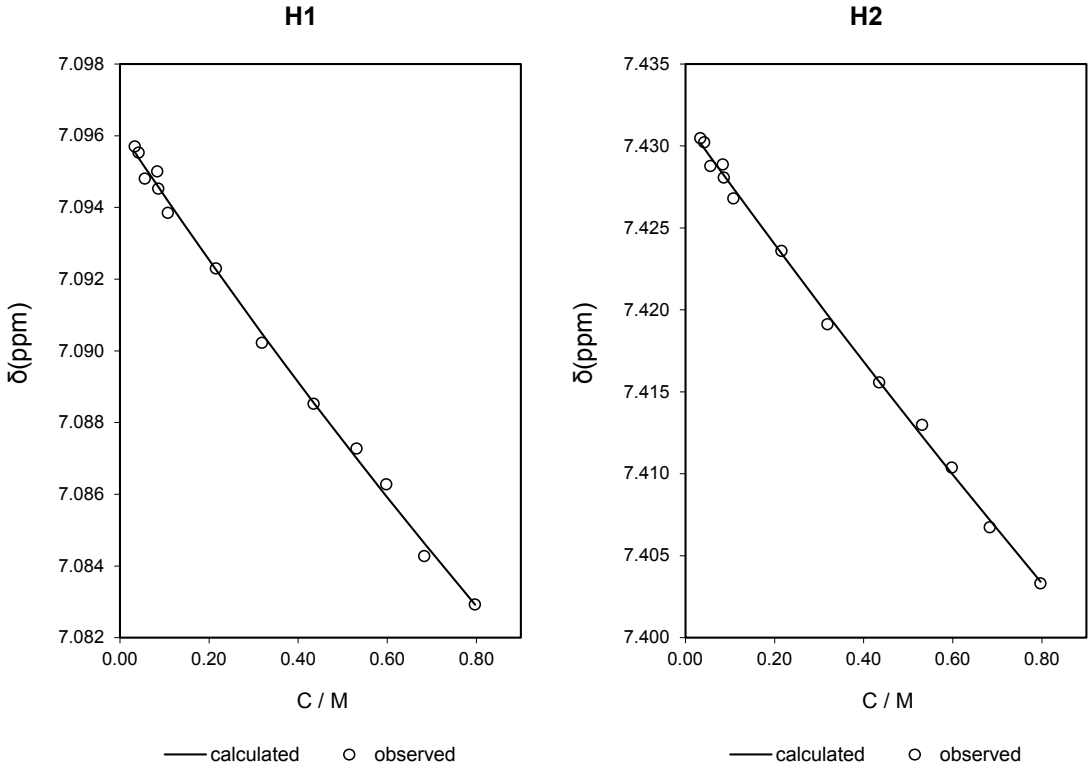

Figure S8. Graphical representation of the fitting results of the calculated chemical shifts, δ, to the experimental data for the NMR dissolution studies of 22-BT in acetone-d_6.

Table S9. ^{1}H NMR results for the dissolution studies of 22-BT in acetonitrile-d_3.

NMR tube	[sample] / mol·dm^{-3}	δ(H1) / ppm	δ(H2) / ppm	δ(H3) / ppm
1	0.5900	7.3384	7.2555	7.0672
	0.4916	7.3417	7.2576	7.0691
	0.4214	7.3445	7.2593	7.0705
	0.3278	7.3475	7.2616	7.0727
	0.2950	7.3487	7.2625	7.0734
	0.2682	7.3498	7.2631	7.0739
2	0.1868	7.3529	7.2655	7.0758
	0.1334	7.3547	7.2668	7.0770
3	0.1916	7.3526	7.2653	7.0756
	0.1597	7.3537	7.2661	7.0764
	0.1198	7.3555	7.2674	7.0773
	0.0958	7.3566	7.2681	7.0782

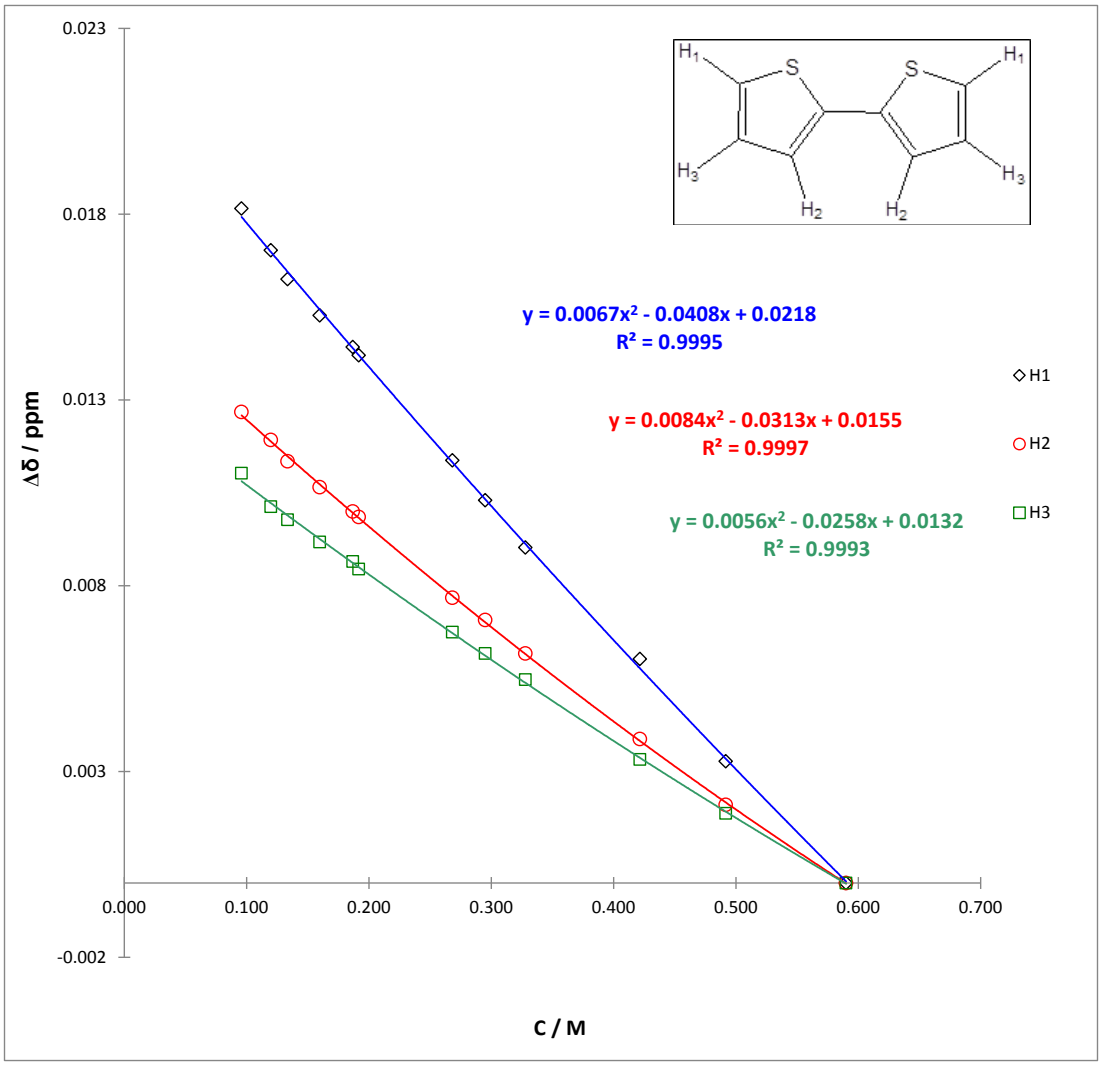

Figure S9. Plot of $\Delta\delta = f$ (sample concentration) for the NMR dissolution studies of 22-BT in acetonitrile-d_3.

Table S10. Results derived from the least squares fitting of equation 2 (in the manuscript) for the NMR dissolution studies of 22-BT in acetonitrile-d_3.

Proton	K_{eq}	$\Sigma(\delta_{calc} - \delta_{exp})^2$
H1	0.076	$1.9 \cdot 10^{-7}$
H2	0.082	$9.9 \cdot 10^{-8}$
H3	0.081	$1.0 \cdot 10^{-7}$

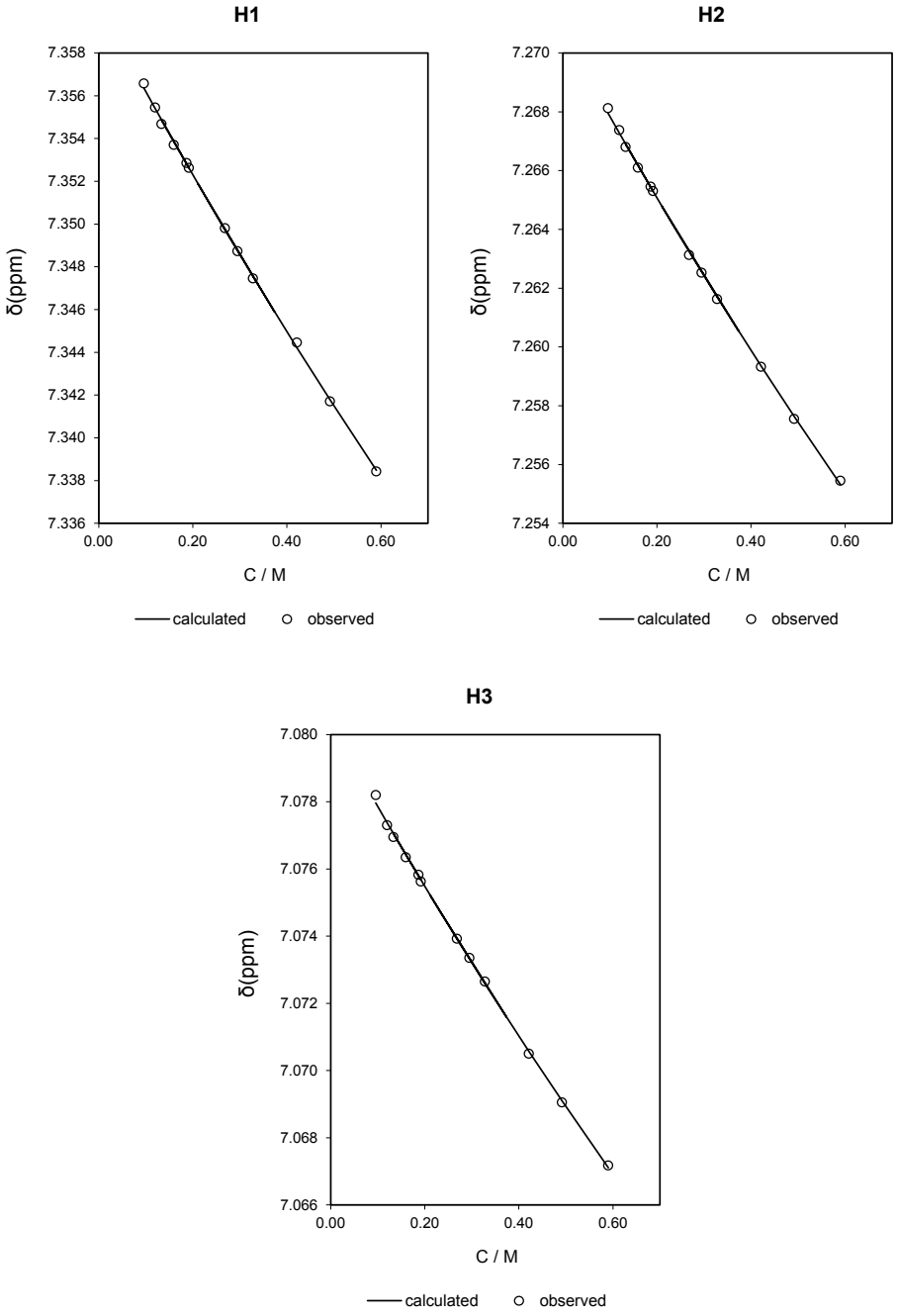

Figure S10. Graphical representation of the fitting results of the calculated chemical shifts, δ, to the experimental data for the NMR dissolution studies of 22-BT in acetonitrile-d_3.

C) 3,3'-Bithiophene (33-BT)

Table S11. ^{1}H NMR results for the dissolution studies of 33-BT in $CDCl_3$.

NMR tube	[sample] / mol·dm^{-3}	δ(H1) / ppm	δ(H2) / ppm
1	0.6275	7.3248	7.3023
	0.5020	7.3340	7.3116
	0.4183	7.3402	7.3184
	0.3585	7.3451	7.3228
	0.3137	7.3486	7.3265
	0.2092	7.3563	7.3338
	0.1673	7.3595	7.3369
	0.1394	7.3615	7.3389
	0.1141	7.3638	7.3412
2	0.0917	7.3653	7.3427
	0.0459	7.3699	7.3469
	0.0306	7.3707	7.3481
	0.0208	7.3715	7.3489

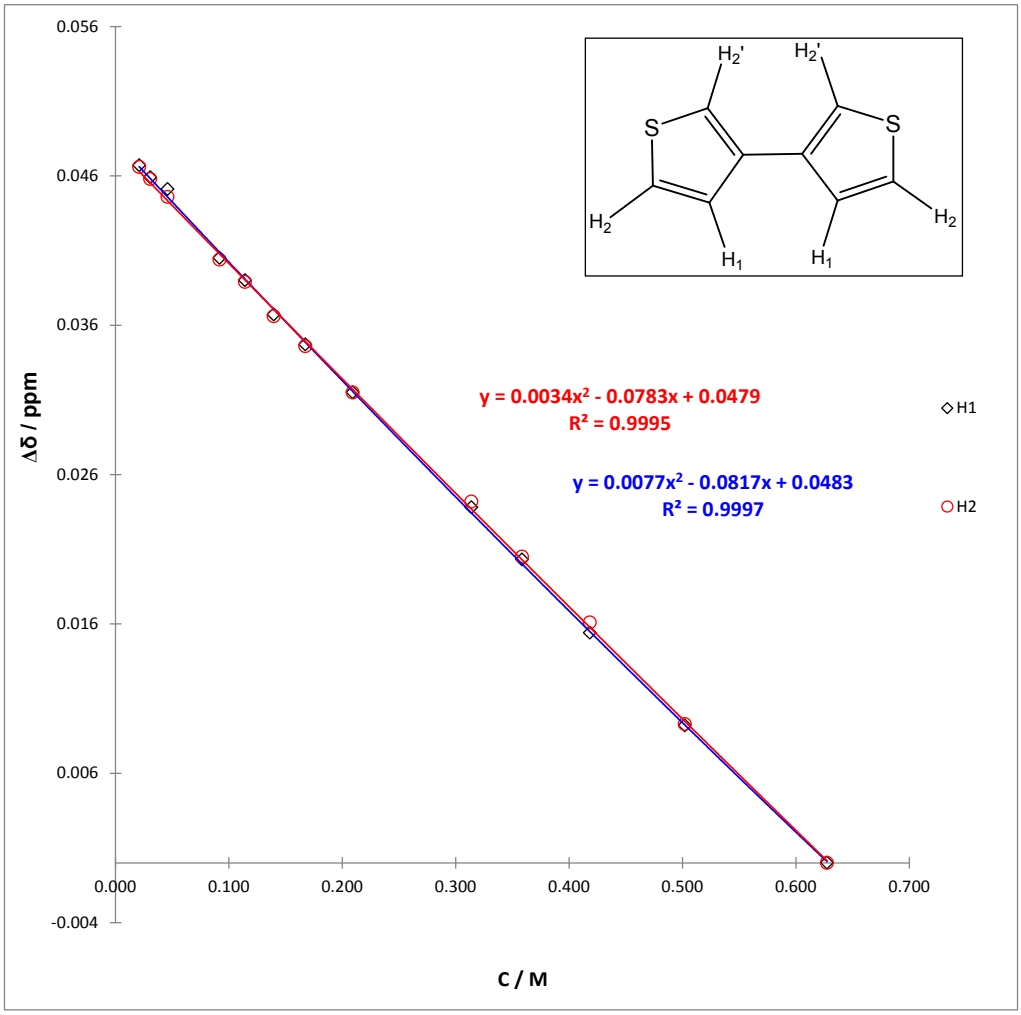

Figure S11. Plot of $\Delta\delta = f$ (sample concentration) for the NMR dissolution studies of 33-BT in $CDCl_3$.

Table S12. Results derived from the least squares fitting of equation 2 (in the manuscript) for the NMR dissolution studies of 33-BT in $CDCl_3$.

Proton	K_{eq}	$\Sigma(\delta_{calc} - \delta_{exp})^2$
H1	0.038	$8.2 \cdot 10^{-7}$
H2	0.024	$1.2 \cdot 10^{-6}$

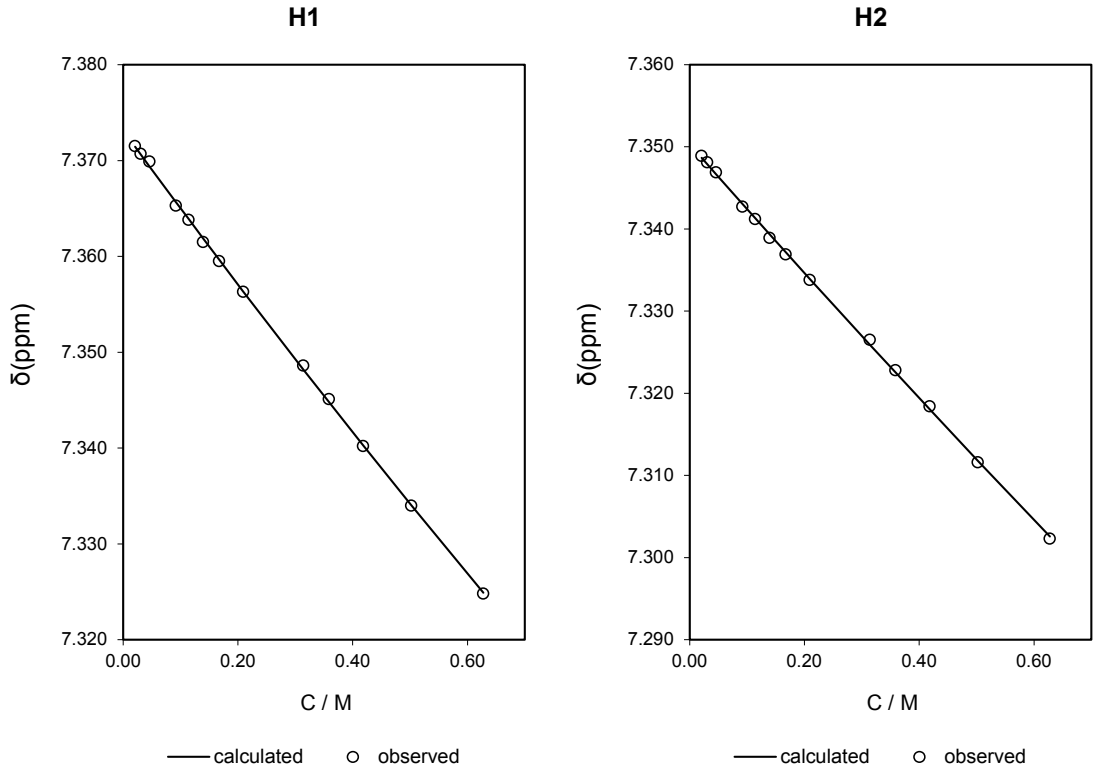

Figure S12. Graphical representation of the fitting results of the calculated chemical shifts, δ, to the experimental data for the NMR dissolution studies of 33-BT in $CDCl_3$.

Table S13. ^{1}H NMR results for the dissolution studies of 33-BT in acetone-d_6.

NMR tube	[sample] / mol·dm^{-3}	δ(H1) / ppm	δ(H2) / ppm
1	0.5268	7.6677	7.5159
	0.4390	7.6711	7.5187
	0.3763	7.6735	7.5202
	0.3293	7.6756	7.5218
	0.2634	7.6774	7.5232
	0.2195	7.6798	7.5252
3	0.0573	7.6869	7.5302
	0.0287	7.6882	7.5315
	0.0191	7.6884	7.5315
	0.0143	7.6890	7.5317

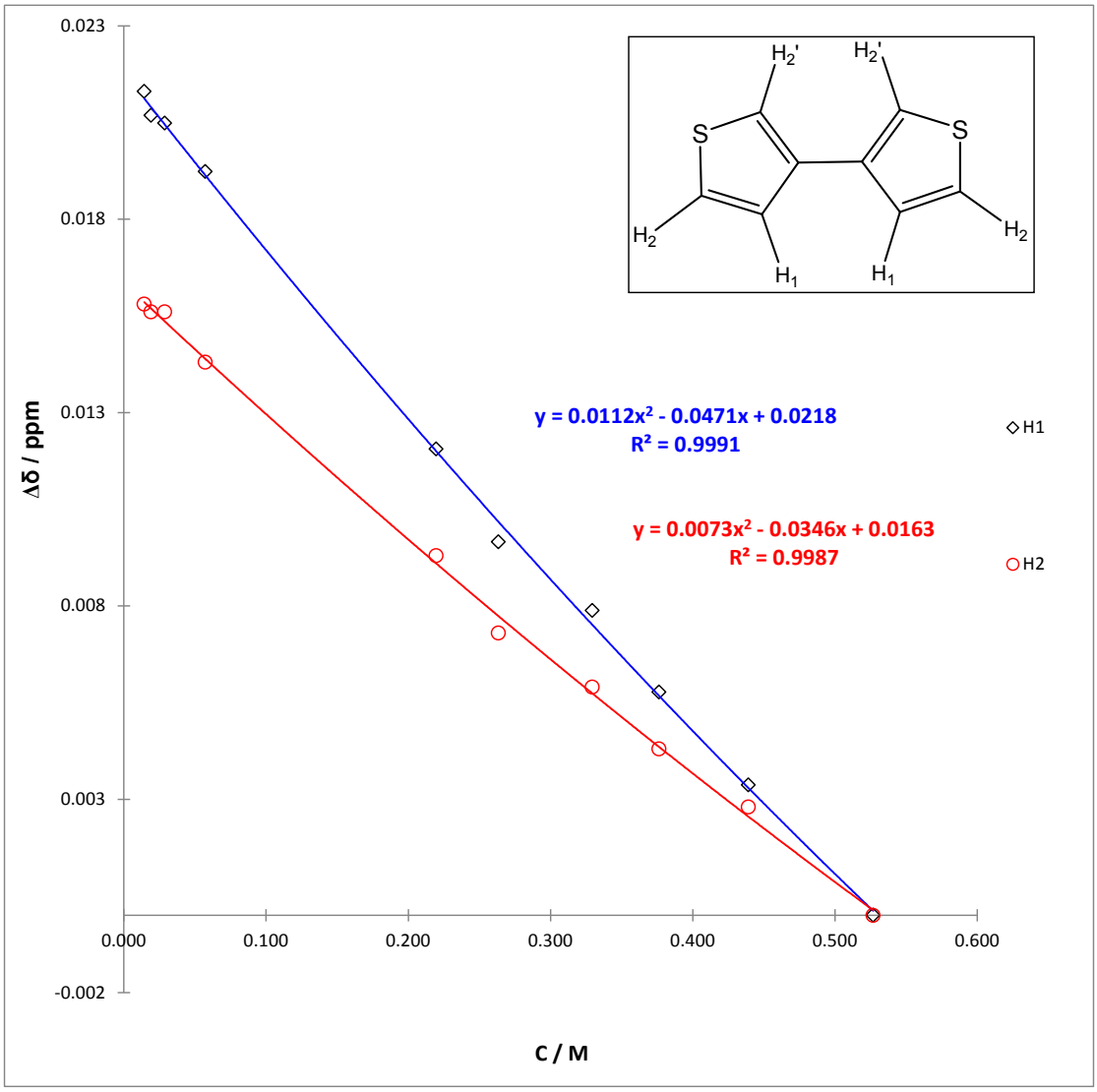

Figure S13. Plot of Δδ = *f* (sample concentration) for the NMR dissolution studies of 33-BT in acetone-d_6.

Table S14. Results derived from the least squares fitting of equation 2 (in the manuscript) for the NMR dissolution studies of 33-BT in acetone-d_6.

Proton	K_{eq}	$\Sigma(\delta_{calc} - \delta_{exp})^2$
H1	0.111	$5.1 \cdot 10^{-7}$
H2	0.096	$4.0 \cdot 10^{-7}$

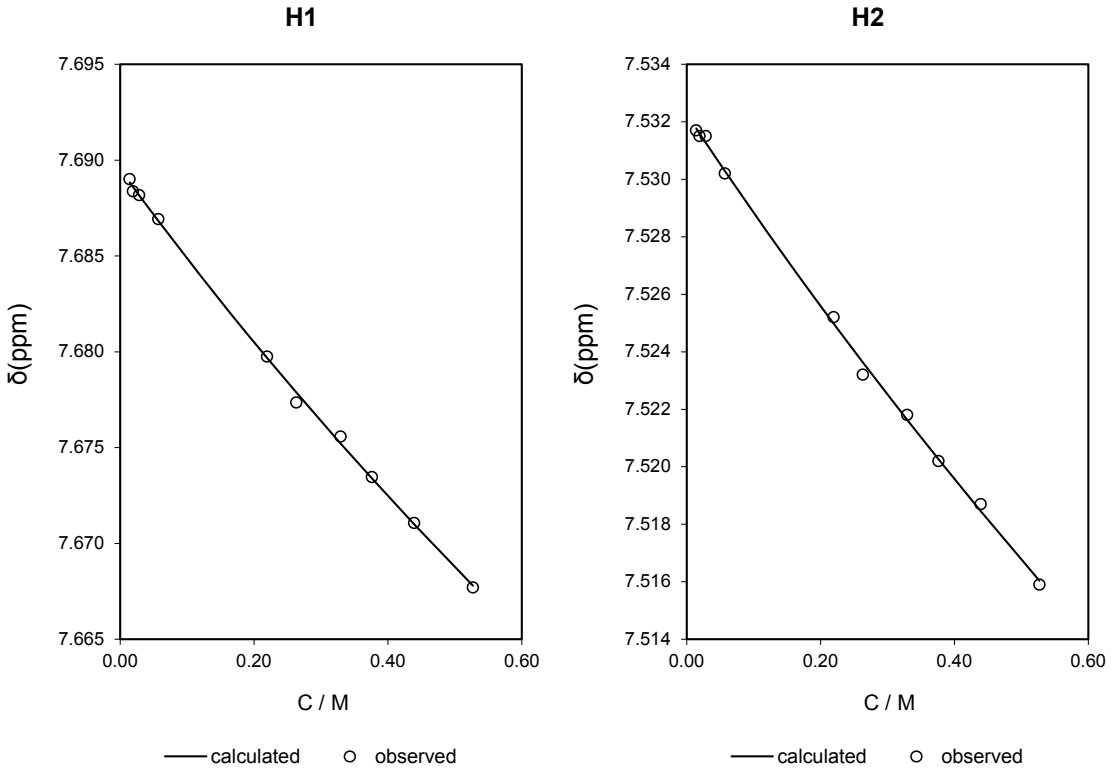

Figure S14. Graphical representation of the fitting results of the calculated chemical shifts, δ, to the experimental data for the NMR dissolution studies of 33-BT in acetone-d_6.

Table S15. ^{1}H NMR results for the dissolution studies of 33-BT in acetonitrile-d_3.

NMR tube	[sample] / mol·dm^{-3}	δ(H1) / ppm	δ(H2) / ppm
1	0.2621	7.5598	7.4670
	0.2184	7.5619	7.4684
	0.1872	7.5635	7.4693
	0.1638	7.5644	7.4700
	0.1456	7.5653	7.4705
	0.1191	7.5668	7.4715
	0.1008	7.5677	---
2	0.1775	7.5639	---
	0.0887	7.5683	---
	0.0634	---	7.4734
3	0.0856	7.5683	7.4727
	0.0713	7.5693	7.4731
	0.0428	7.5707	7.4742
	0.0306	7.5713	---

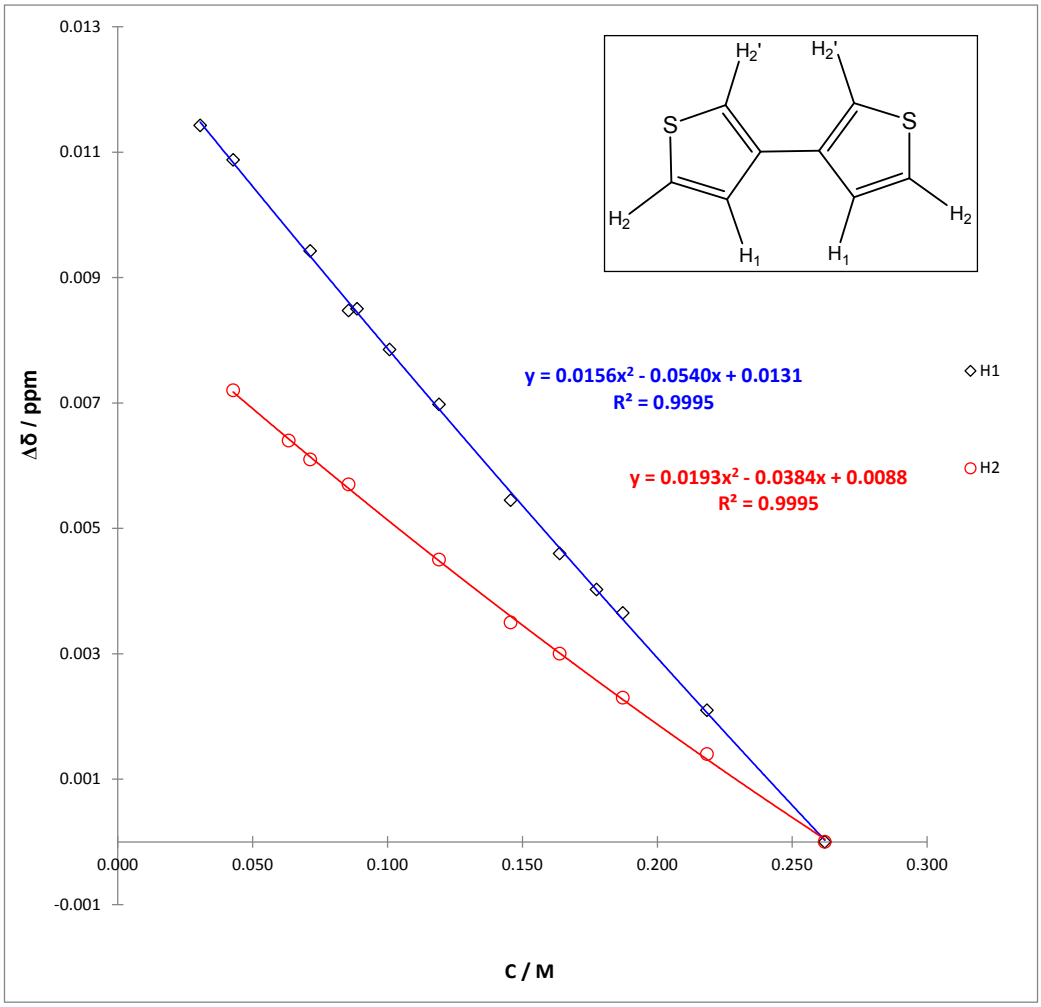

Figure S15. Plot of $\Delta\delta = f$ (sample concentration) for the NMR dissolution studies of 33-BT in acetonitrile-d_3.

Table S16. Results derived from the least squares fitting of equation 2 (in the manuscript) for the NMR dissolution studies of 33-BT in acetonitrile-d_3.

Proton	K_{eq}	$\Sigma(\delta_{calc} - \delta_{exp})^2$
H1	0.160	$8.6 \cdot 10^{-8}$
H2	0.156	$4.5 \cdot 10^{-8}$

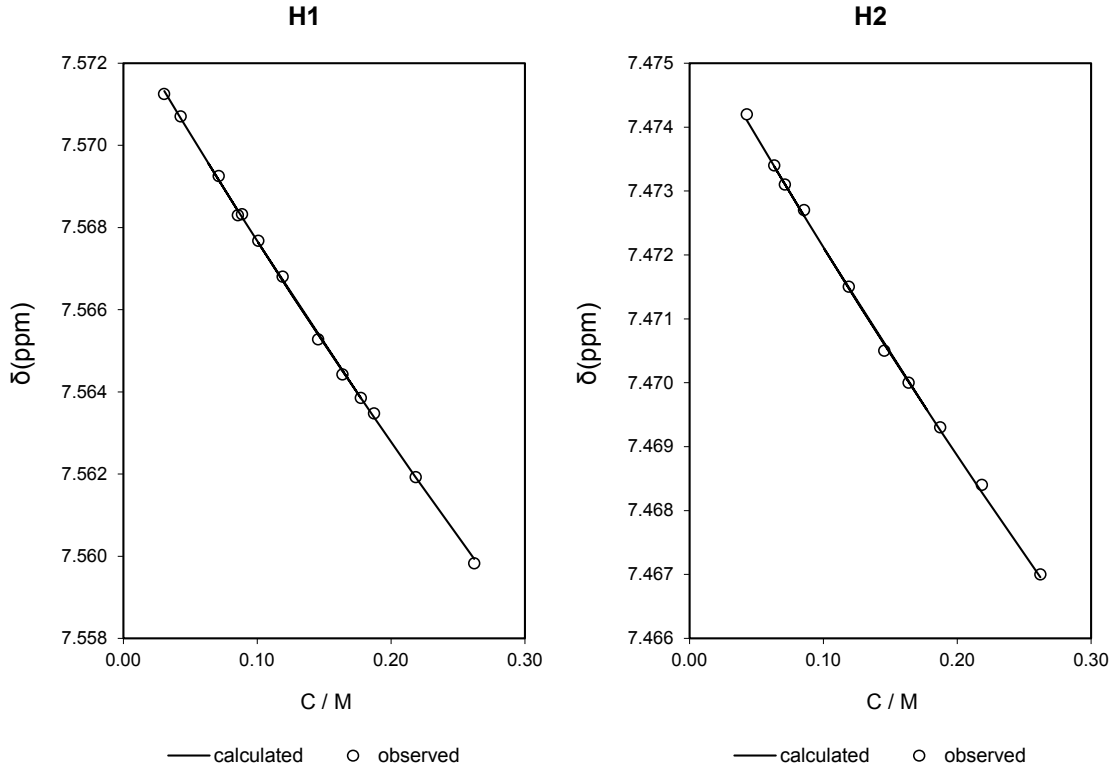

Figure S16. Graphical representation of the fitting results of the calculated chemical shifts, δ, to the experimental data for the NMR dissolution studies of 33-BT in acetonitrile-d_3.

D) 2,2',5',2''-Terthiophene (2252-TT)

Table S17. ^{1}H NMR results for the dissolution studies of 2252-TT in $CDCl_3$.

NMR tube	[sample] / mol·dm^{-3}	δ(H1) / ppm	δ(H2) / ppm	δ(H3) / ppm	δ(H4) / ppm
1	0.4242	7.1780	6.9844	7.1406	7.0426
	0.3394	7.1863	6.9918	7.1473	7.0497
	0.2828	7.1919	6.9969	7.1517	7.0542
	0.2424	7.1962	7.0008	7.1551	7.0582
	0.2121	7.1994	7.0040	7.1579	7.0612
	0.1414	7.2072	7.0107	7.1639	7.0680
	0.1212	7.2089	7.0127	7.1657	7.0695
	0.1060	7.2102	7.0137	7.1665	7.0708
	0.0893	---	---	---	7.0724
	0.0771	7.2134	7.0168	7.1691	7.0736
2	0.0196	7.2209	7.0235	7.1752	7.0804
	0.0088	7.2220	7.0246	7.1763	7.0812

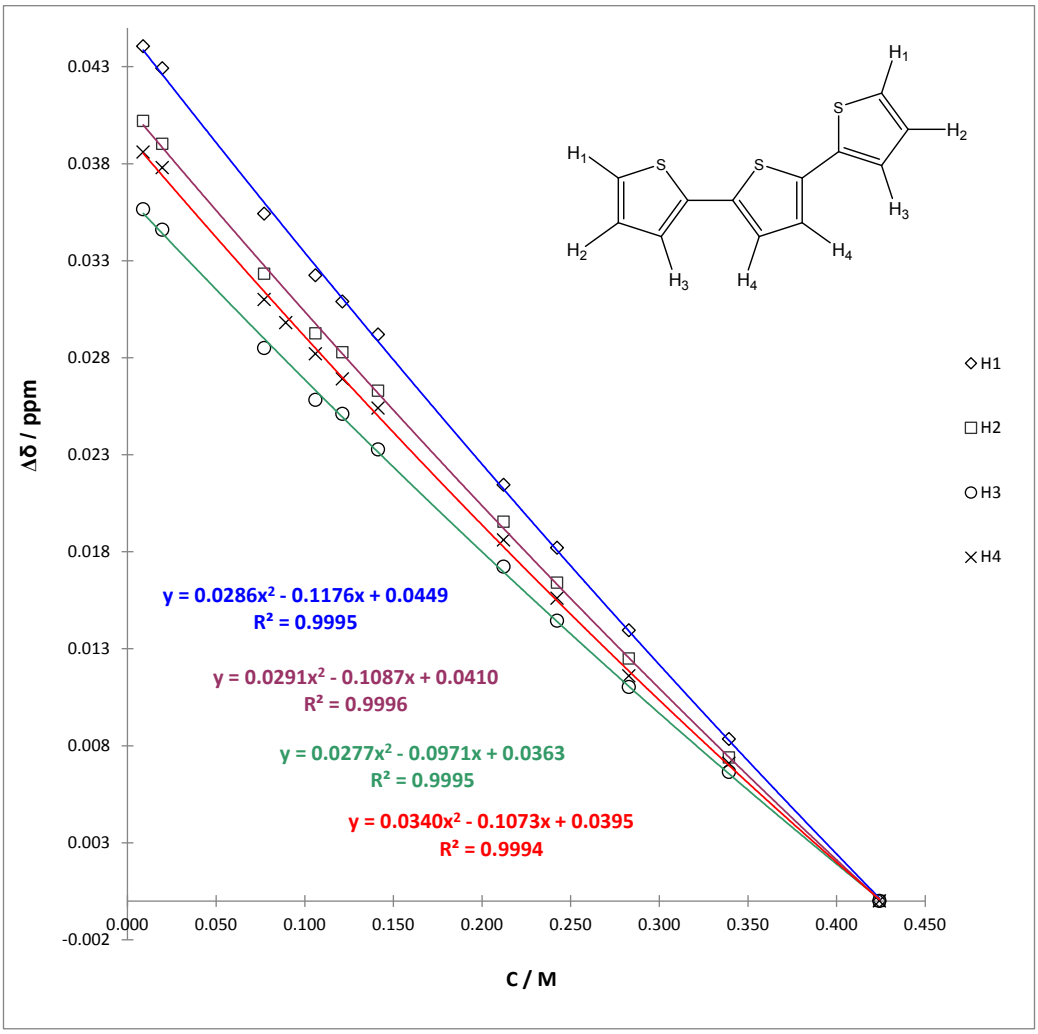

Figure S17. Plot of $\Delta\delta = f$ (sample concentration) for the NMR dissolution studies of 2252-TT in $CDCl_3$.

Table S18. Results derived from the least squares fitting of equation 2 (in the manuscript) for the NMR dissolution studies of 2252-TT in $CDCl_3$.

Proton	K_{eq}	$\Sigma(\delta_{calc} - \delta_{exp})^2$
H1	0.107	$8.9 \cdot 10^{-7}$
H2	0.121	$6.1 \cdot 10^{-7}$
H3	0.132	$6.4 \cdot 10^{-7}$
H4	0.151	$8.9 \cdot 10^{-7}$

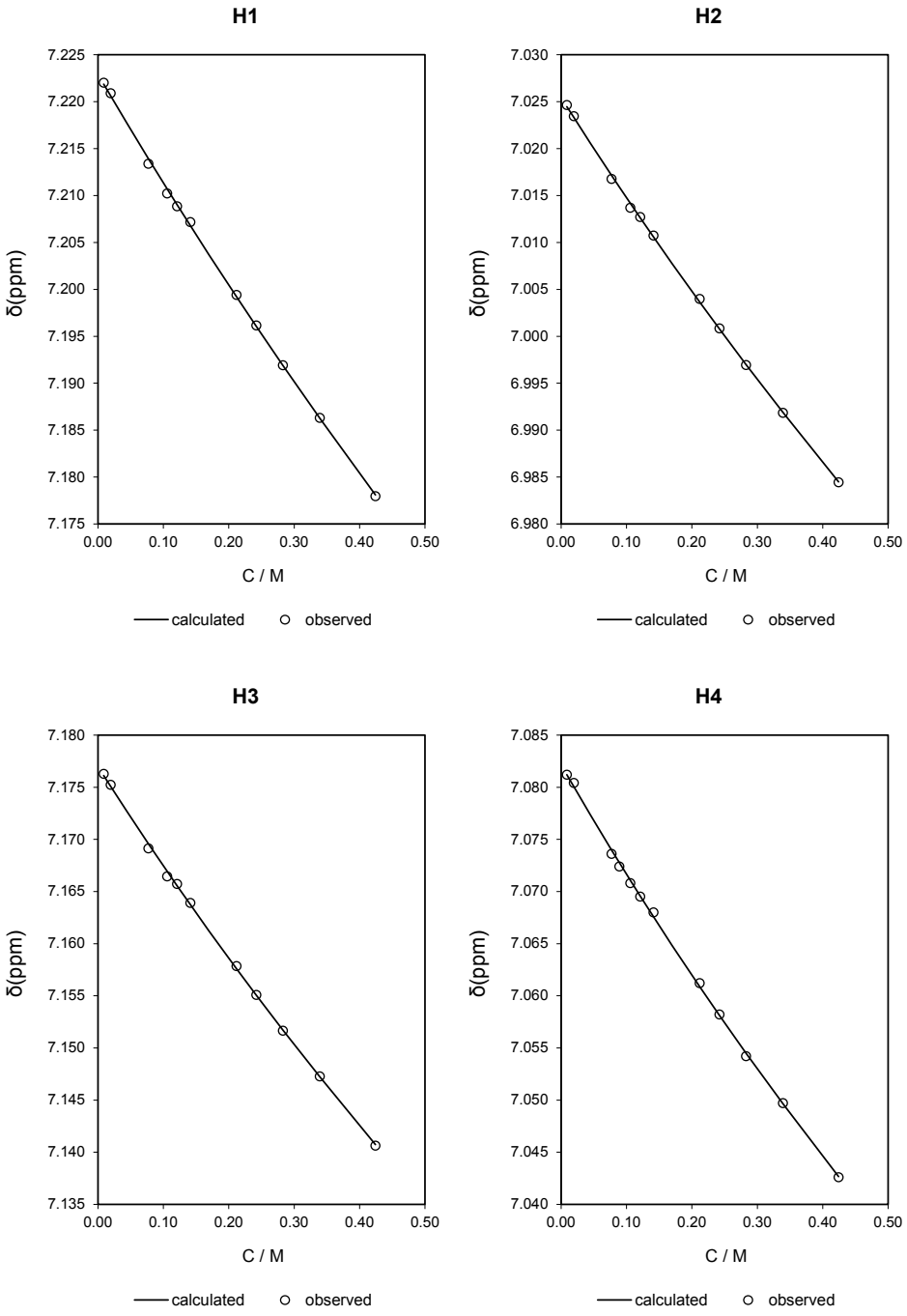

Figure S18. Graphical representation of the fitting results of the calculated chemical shifts, δ, to the experimental data for the NMR dissolution studies of 2252-TT in $CDCl_3$.

Table S19. ^{1}H NMR results for the dissolution studies of 2252-TT in acetone-d_6.

NMR tube	[sample] / mol·dm^{-3}	δ(H1) / ppm	δ(H2) / ppm	δ(H3) / ppm	δ(H4) / ppm
	0.3318	7.4303	7.0905	7.2962	7.2078
	0.2765	7.4339	---	7.2991	---
	0.2370	7.4370	7.0950	7.3021	7.2148
	0.2074	7.4396	7.0966	7.3045	7.2175
1	0.1843	7.4411	7.0979	7.3059	7.2190
	0.1508	7.4439	7.0995	7.3084	7.2218
	0.1185	7.4468	7.1018	7.3112	7.2248
	0.0976	7.4486	7.1032	7.3130	7.2266
	0.0830	7.4505	7.1044	7.3147	7.2287
	0.0371	7.4547	7.1073	7.3185	7.2331
2	0.0297	7.4551	7.1078	7.3192	7.2342
	0.0165	7.4566	7.1086	7.3204	7.2350
3	0.0057	7.4577	7.1092	7.3213	7.2360

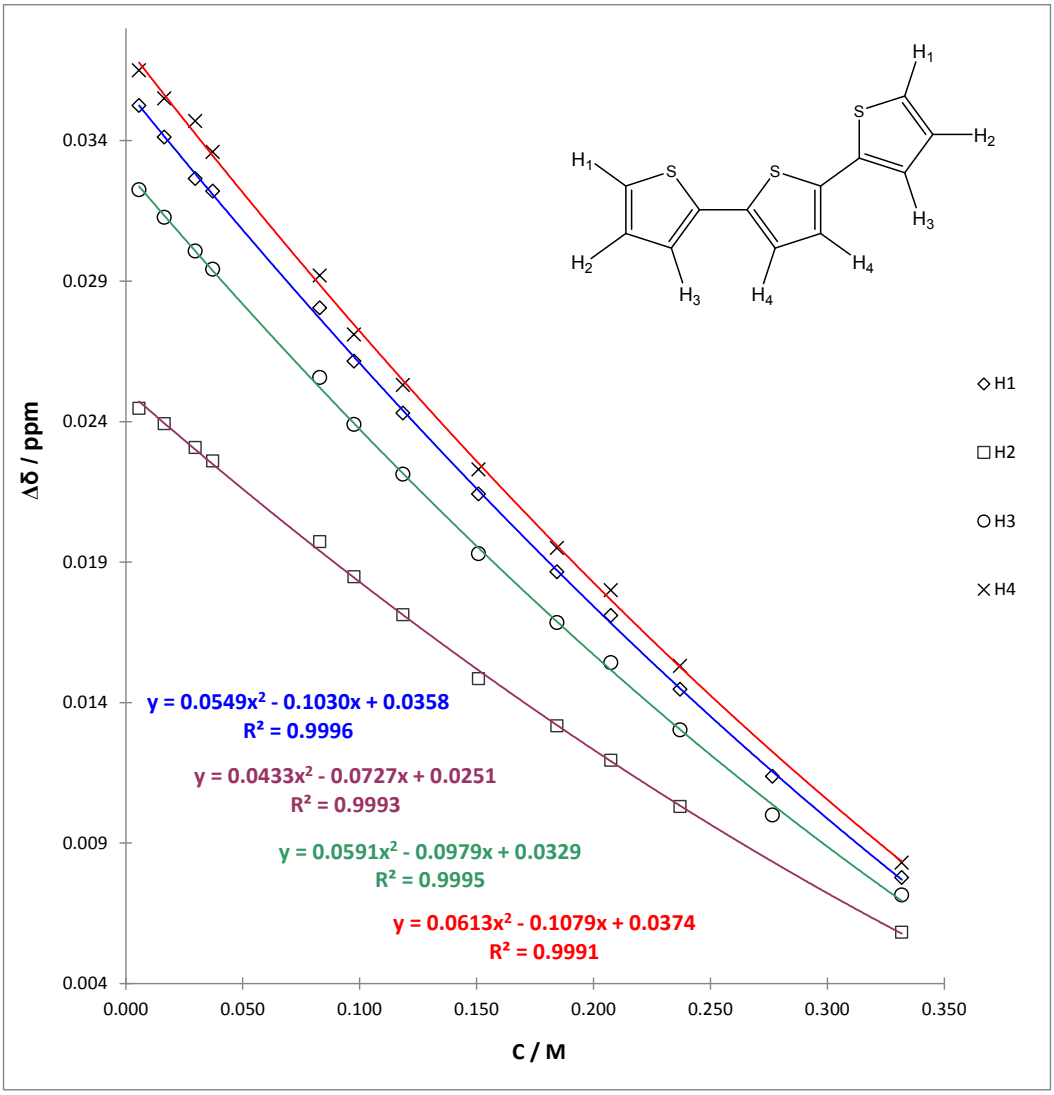

Figure S19. Plot of $\Delta\delta = f$ (sample concentration) for the NMR dissolution studies of 2252-TT in acetone-d_6.

Table S20. Results derived from the least squares fitting of equation 2 (in the manuscript) for the NMR dissolution studies of 2252-TT in acetone-d_6.

Proton	K_{eq}	$\Sigma(\delta_{calc} - \delta_{exp})^2$
H1	0.273	$4.0 \cdot 10^{-7}$
H2	0.316	$3.6 \cdot 10^{-7}$
H3	0.324	$5.8 \cdot 10^{-7}$
H4	0.306	$7.9 \cdot 10^{-7}$

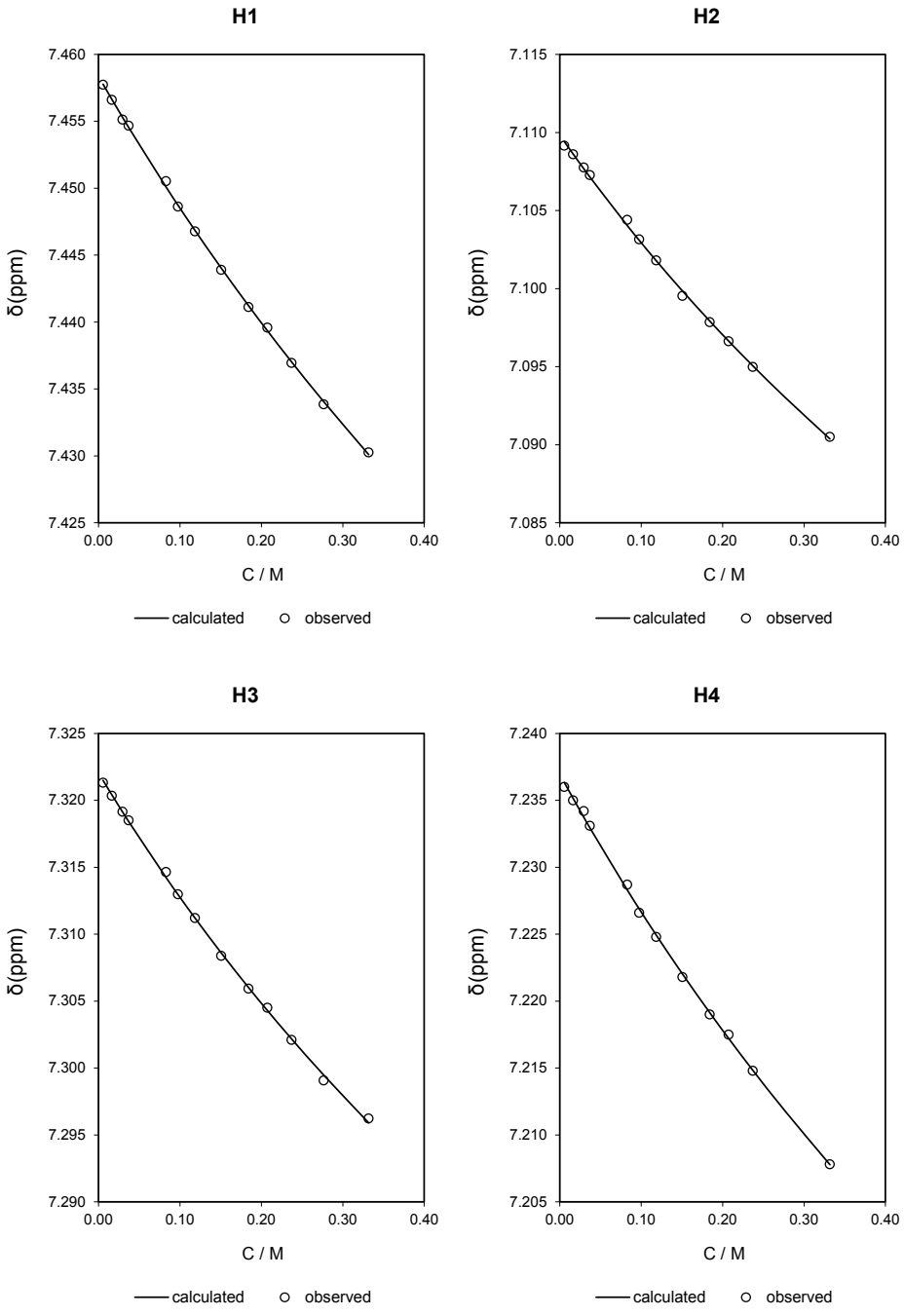

Figure S20. Graphical representation of the fitting results of the calculated chemical shifts, δ, to the experimental data for the NMR dissolution studies of 2252-TT in acetone-d_6.

E) 3,3‴-Dihexyl-2,2′:5′,2″:5″,2‴-quaterthiophene (DH-α-QT)

Table S21. ^{1}H NMR results for the dissolution studies of DH-α-QT in $CDCl_3$.

NMR tube	[sample] / mol·dm^{-3}	δ(H1) / ppm	δ(H2) / ppm	δ(H4) / ppm
1	0.2873	7.1428	7.0995	6.9146
	0.2394	7.1486	7.1037	6.9187
	0.1795	7.1563	7.1093	6.9240
	0.1436	7.1613	7.1133	6.9278
	0.1026	7.1672	7.1176	6.9320
2	0.1847	7.1551	7.1084	6.9235
	0.1539	7.1589	7.1114	6.9260
	0.0923	7.1676	7.1179	6.9322
	0.0660	7.1722	7.1215	6.9356
3	0.1358	7.1618	7.1135	6.9280
	0.0849	7.1690	7.1190	6.9334
	0.0566	7.1731	7.1220	6.9359
	0.0485	7.1742	7.1227	6.9369

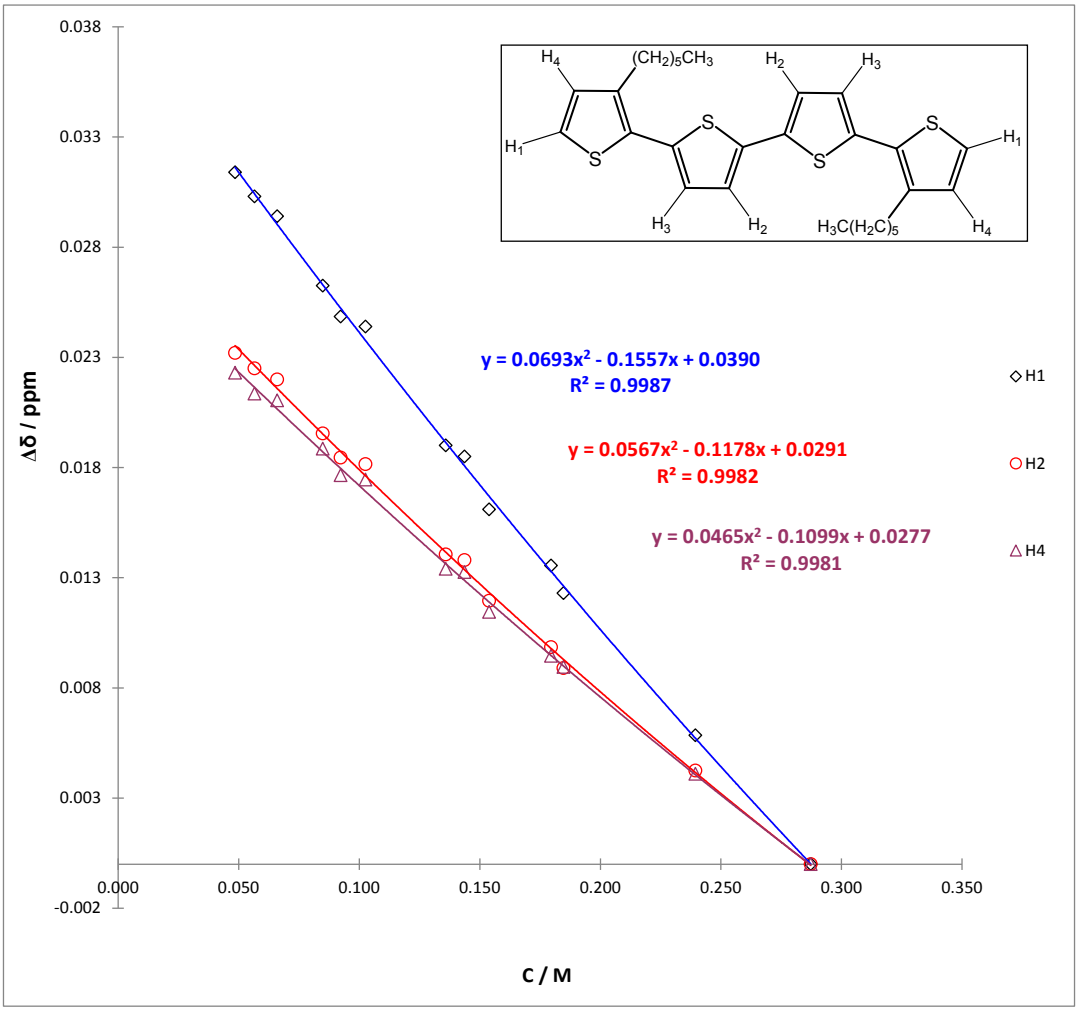

Figure S21. Plot of $\Delta\delta = f$ (sample concentration) for the NMR dissolution studies of DH-α-QT in $CDCl_3$.

Table S22. Results derived from the least squares fitting of equation 2 (in the manuscript) for the NMR dissolution studies of DH-α-QT in $CDCl_3$.

Proton	K_{eq}	$\Sigma(\delta_{calc} - \delta_{exp})^2$
H1	0.212	$1.5 \cdot 10^{-6}$
H2	0.231	$1.2 \cdot 10^{-6}$
H4	0.195	$1.1 \cdot 10^{-6}$

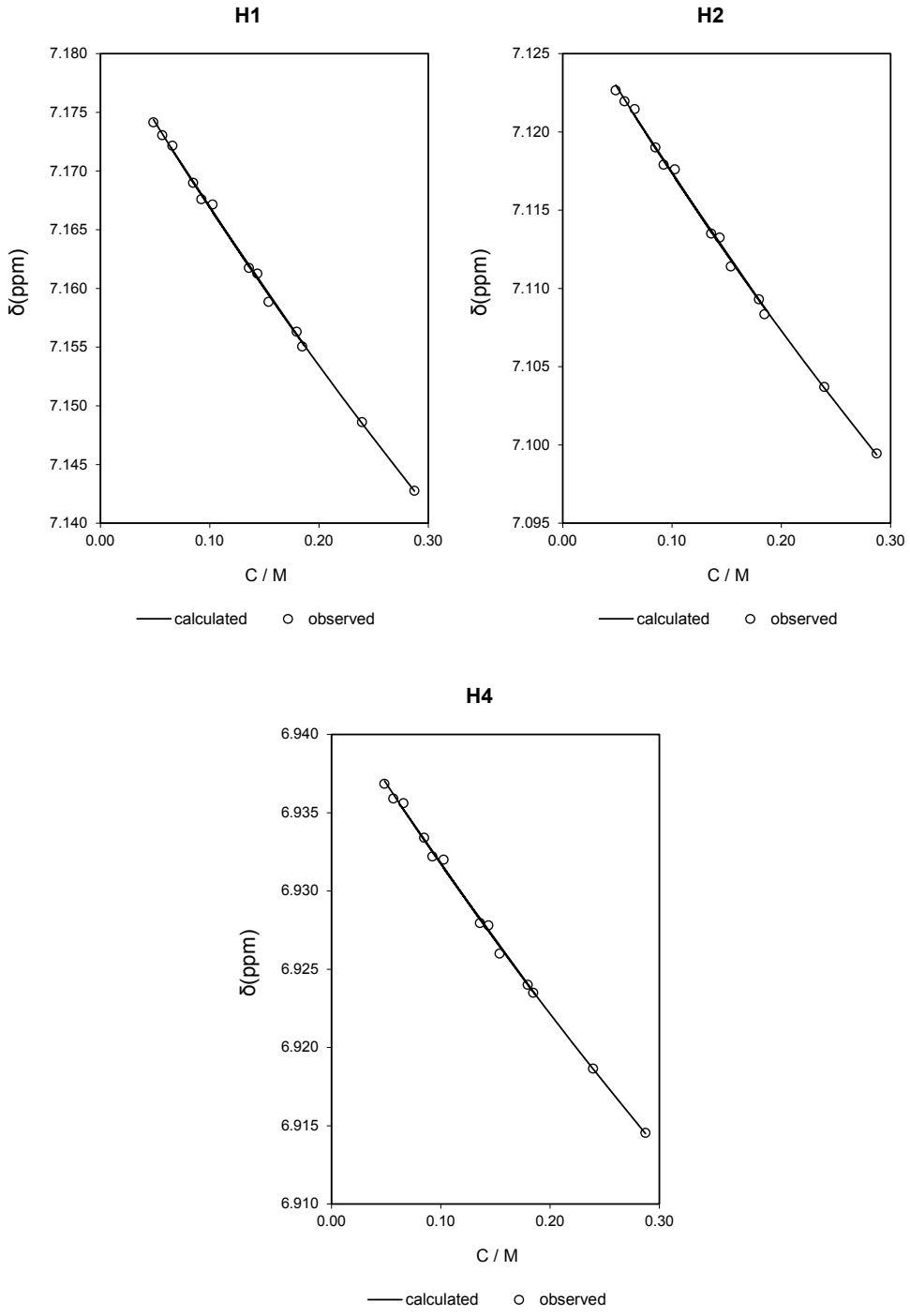

Figure S22. Graphical representation of the fitting results of the calculated chemical shifts, δ, to the experimental data for the NMR dissolution studies of DH-α-QT in $CDCl_3$.

Table S23. ^{1}H NMR results for the dissolution studies of DH-α-QT in acetone-d_6.

NMR tube	[sample] / mol·dm^{-3}	δ(H2) / ppm	δ(H3) / ppm	δ(H4) / ppm
1	0.1916	7.2661	7.1150	7.0344
	0.1597	7.2746	7.1217	7.0403
	0.1369	7.2822	7.1273	7.0454
	0.1198	7.2872	7.1309	7.0487
	0.0958	7.2955	7.1370	7.0539
	0.0684	7.3053	7.1442	7.0601
2	0.0531	7.3107	7.1481	7.0634
	0.0379	7.3165	7.1525	7.0672
3	0.0629	7.3066	7.1450	7.0608
	0.0440	7.3142	7.1507	7.0657
	0.0314	7.3193	7.1545	7.0689

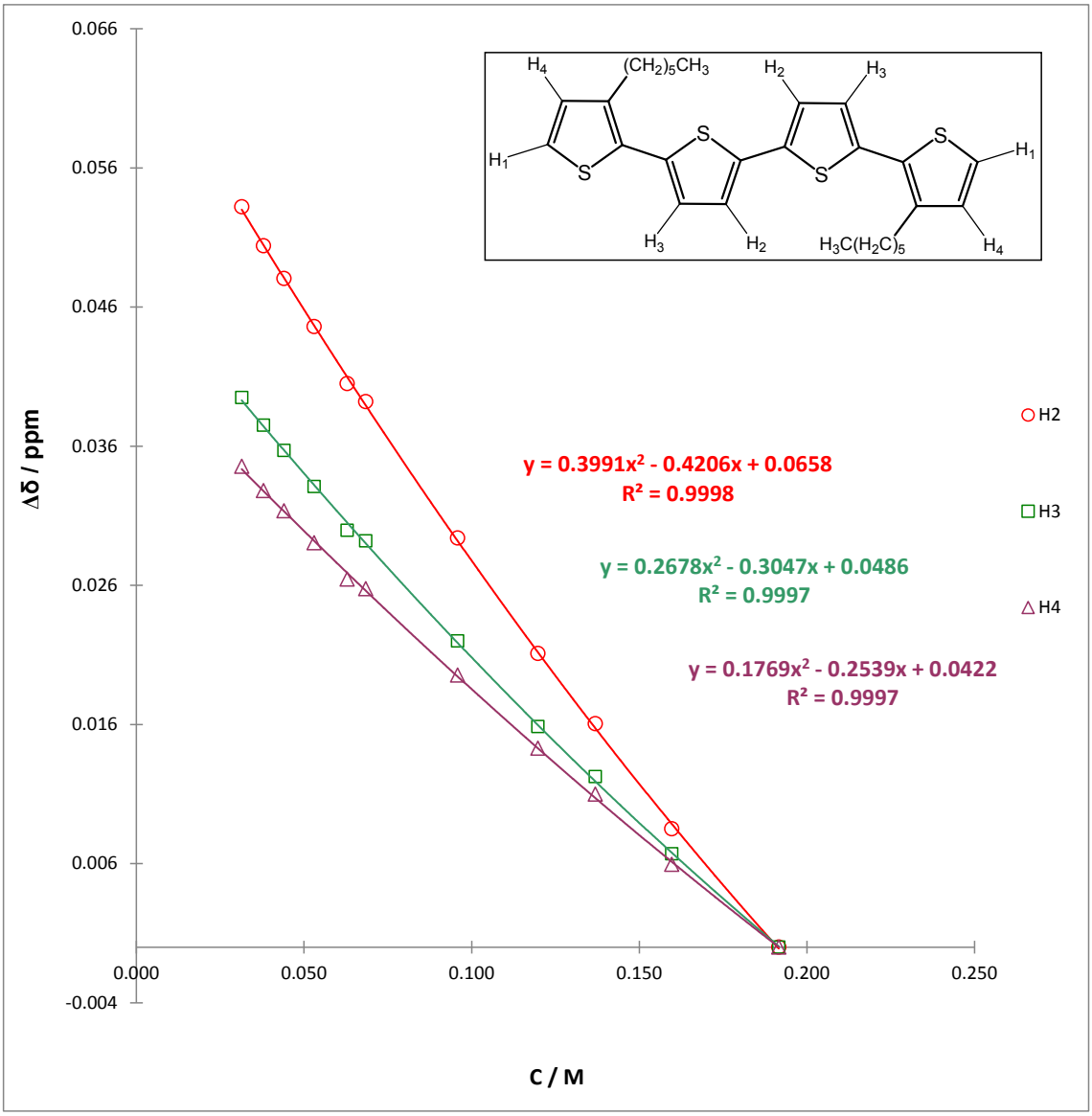

Figure S23. Plot of Δδ = *f* (sample concentration) for the NMR dissolution studies of DH-α-QT in acetone-d_6.

Table S24. Results derived from the least squares fitting of equation 2 (in the manuscript) for the NMR dissolution studies of DH-α-QT in acetone-d_6.

Proton	K_{eq}	$\Sigma(\delta_{calc} - \delta_{exp})^2$
H2	0.558	$6.4 \cdot 10^{-7}$
H3	0.506	$4.8 \cdot 10^{-7}$
H4	0.354	$3.6 \cdot 10^{-7}$

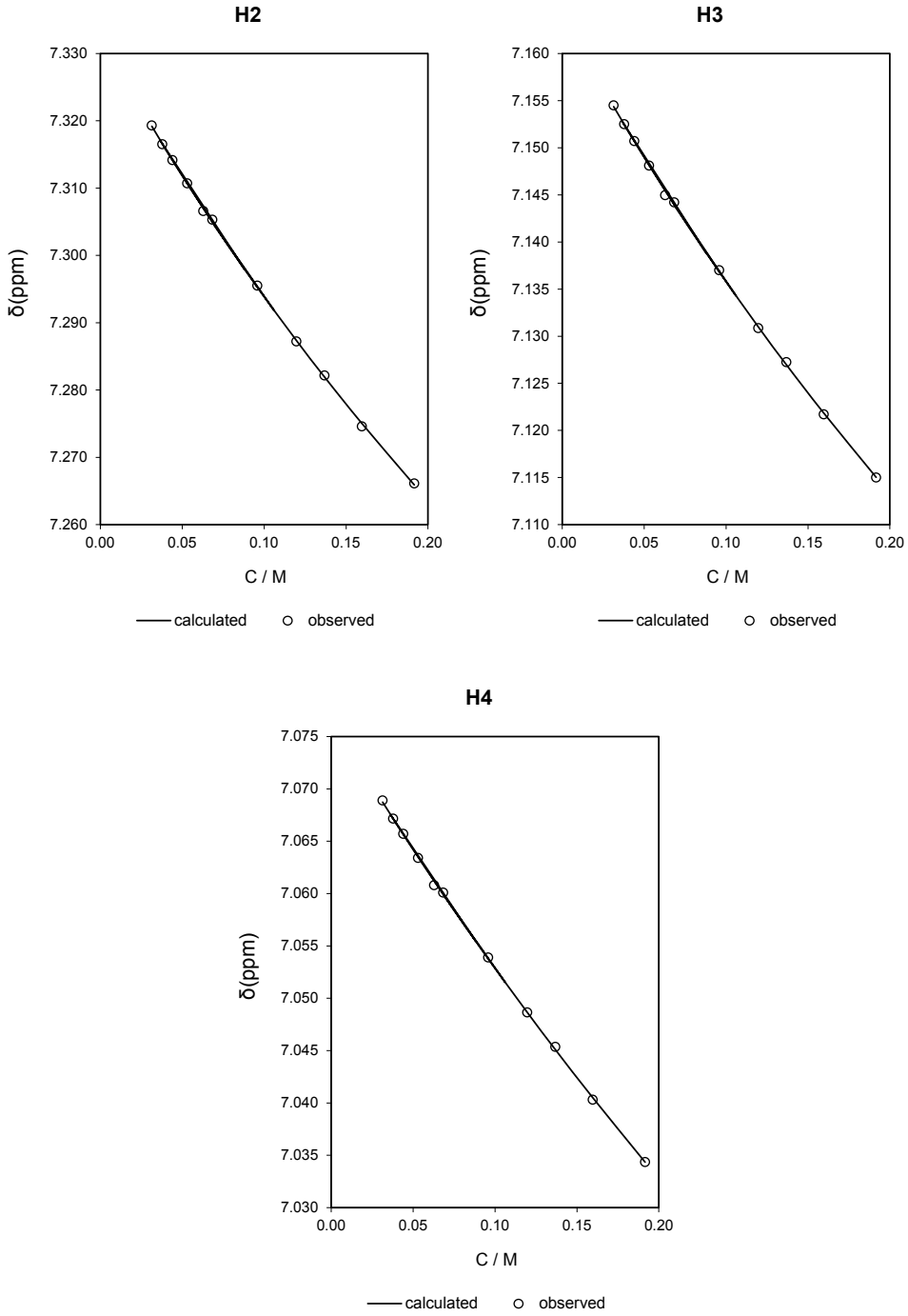

Figure S24. Graphical representation of the fitting results of the calculated chemical shifts, δ, to the experimental data for the NMR dissolution studies of DH-α-QT in acetone-d_6.

F) 3,3‴-Didodecyl-2,2′:5′,2″:5″,2‴−quaterthiophene (DD-α-QT)

Table S25. ^{1}H NMR results for the dissolution studies of DD-α-QT in $CDCl_3$.

NMR tube	[sample] / mol·dm^{-3}	δ(H1) / ppm	δ(H2) / ppm	δ(H3) / ppm	δ(H4) / ppm
	0.1868	7.1504	7.1034	7.0014	6.9196
	0.1557	7.1545	7.1065	7.0033	6.9225
	0.1334	7.1587	7.1093	7.0060	6.9257
1	0.1168	7.1607	7.1108	7.0071	6.9270
	0.0934	7.1647	7.1136	7.0098	6.9299
	0.0849	7.1657	7.1147	7.0099	6.9305
	0.0667	7.1689	7.1165	7.0114	6.9326
	0.1001	7.1634	7.1131	7.0087	6.9290
2	0.0715	7.1678	7.1163	7.0113	6.9321
	0.0358	7.1741	7.1205	7.0147	6.9364
	0.0686	7.1687	7.1164	7.0114	6.9325
3	0.0429	7.1729	7.1201	7.0140	6.9357
	0.0312	7.1747	7.1211	7.0153	6.9369

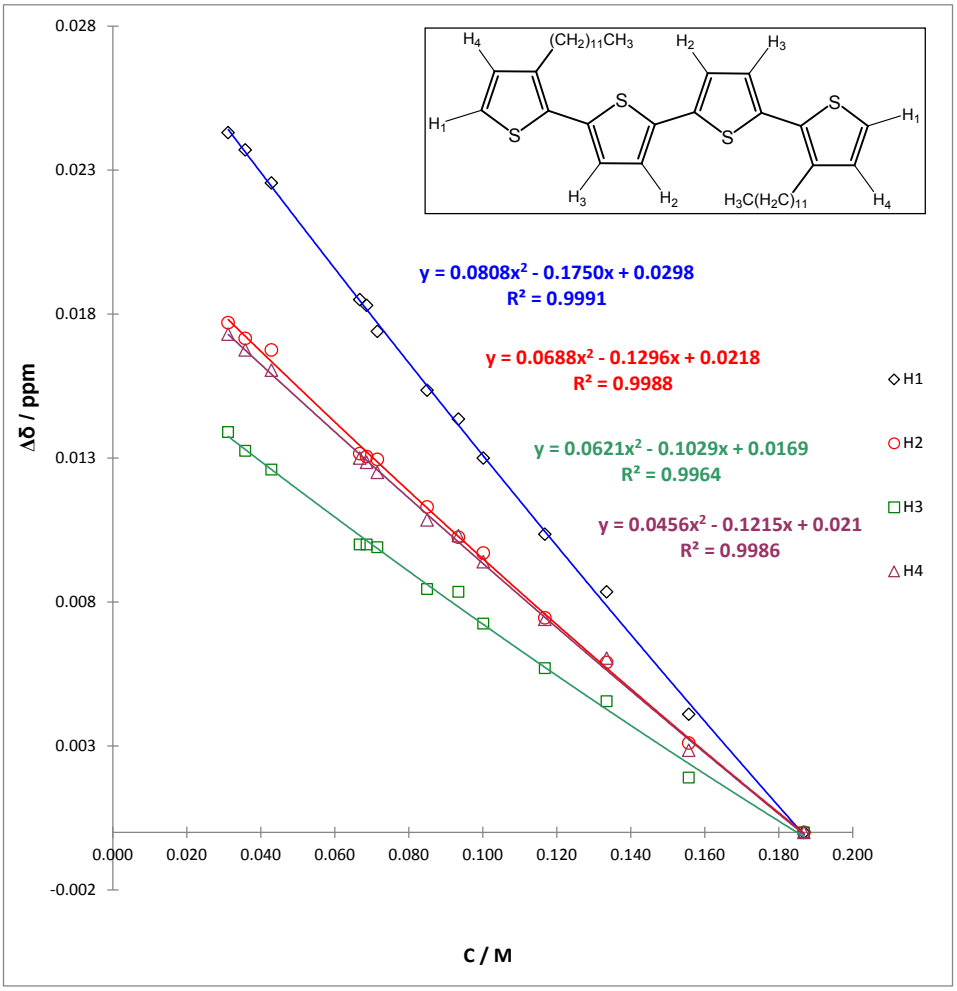

Figure S25. Plot of $\Delta\delta = f$ (sample concentration) for the NMR dissolution studies of DD-α-QT in $CDCl_3$.

Table S26. Results derived from the least squares fitting of equation 2 (in the manuscript) for the NMR dissolution studies of DD-α-QT in $CDCl_3$.

Proton	K_{eq}	$\Sigma(\delta_{calc} - \delta_{exp})^2$
H1	0.201	$6.1 \cdot 10^{-7}$
H2	0.239	$4.2 \cdot 10^{-7}$
H3	0.281	$7.7 \cdot 10^{-7}$
H4	0.167	$4.6 \cdot 10^{-7}$

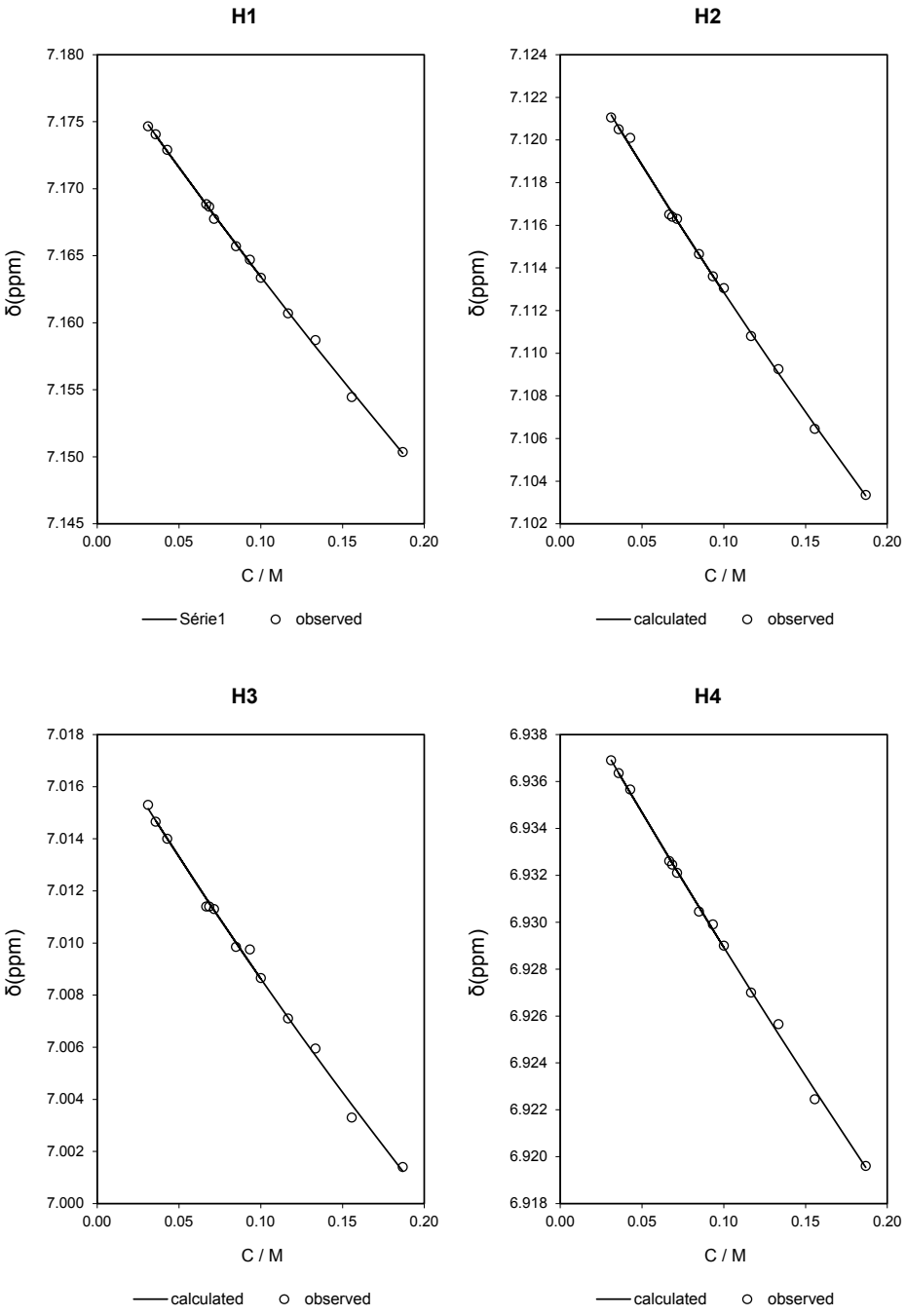

Figure S26. Graphical representation of the fitting results of the calculated chemical shifts, δ, to the experimental data for the NMR dissolution studies of DD-α-QT in $CDCl_3$.

Table S27. ^{1}H NMR dissolution results respecting the alkyl protons of the α-quaterthiophene alkyl derivatives for the solutions of highest and lowest sample concentration in the given solvents.

Compound	[sample] / mol·dm^{-3}	δ(CH_2)$_1$ / ppm [a]	δ(CH_2)$_2$ / ppm [b]	δ(CH_2)$_{mid}$ / ppm [c]	δ(CH_3) / ppm [d]
DH-α-QT ($CDCl_3$)	0.2873	2.7664	1.6381	1.3162	0.8803
	0.0485	2.7776	1.6481	1.3239	0.8854
	Δδ / ppm	**0.0112**	**0.0100**	**0.0077**	**0.0051**
DH-α-QT (acetone-d_6)	0.1916	2.8180	1.6711	1.3368	0.8889
	0.0314	2.8406	1.6897	1.3522	0.8978
	Δδ / ppm	**0.0226**	**0.0186**	**0.0154**	**0.0089**
DD-α-QT ($CDCl_3$)	0.1868	2.7685	1.6406	1.2478	0.8689
	0.0312	2.7764	1.6475	1.2505	0.8711
	Δδ / ppm	**0.0079**	**0.0069**	**0.0027**	**0.0022**

[a] Respecting the protons of the first CH_2 group of the alkyl chain relative to the α-quaterthiophene unit.
[b] Respecting the protons of the second CH_2 group of the alkyl chain.
[c] Respecting the protons of the others CH_2 groups of the chain. NMR signal is an unresolved multiplet.
[d] Respecting the protons of the final CH_3 group of the alkyl chain.

In our analysis we deal mainly with variations in the chemical shifts, Δδ, between spectra recorded at very similar conditions and during the same experimental run; for instance, figure 3 in the manuscript presents Δδ = f ([OT]). Hence, despite each individual chemical shift cannot be known to such accuracy (as implied by the quantity of significant figures in the reported chemical shifts in these tables) its variation with concentration under the same conditions can, and using this data with less significant figures in the non-linear fitting used to determine K_{ass} (see experimental section) would result in significant discrepancies in the calculated values.

- Calculation of uncertainties in K_{ass} and $\Delta_{ass}G_m^0$

The final result of K_{ass} is presented as $\langle K_{ass} \rangle \pm \sigma_m(K_{ass})$, where $\sigma_m(K_{ass})$ is the standard deviation of the mean, calculated as:

$$\sigma_m(K_{ass}) = \sigma(K_{ass}) / n^{1/2} \qquad \text{(S1.1)}$$

where $\sigma(K_{ass})$ is the corrected sample standard deviation, and n is the number of concordant values used for the calculation of $\langle K_{ass} \rangle$.

The error of $\Delta_{ass}G_m^0$ was calculated by applying the formulas of propagation of uncertainty to the equation: $\Delta_{ass}G_m^0 = -R \cdot T \cdot \ln(K_{ass})$, resulting in the following expression for $\sigma(\Delta_{ass}G_m^0)$:

$$\sigma(\Delta_{ass}G_m^0) = R \cdot T \cdot (\sigma_m(K_{ass}) / \langle K_{ass} \rangle) \quad \text{(S1.2)}$$

Since only one value of K_{ass} could be determined for thiophene in acetone-d_6, $\sigma_m(K_{ass})$ was considered to be 0.040, taken as the value of $\sigma_m(K_{ass})$ that corresponds to the maximum $\%(\text{error})(\Delta_{ass}G_m^0)$ obtained for all the compounds studied, where: $\%(\text{error})(\Delta_{ass}G_m^0) = \sigma(\Delta_{ass}G_m^0) / (\Delta_{ass}G_m^0) \cdot 100$.

Section S2. Computational details

Table S28. Electronic energies for the two conformations of 2,2'-biothiophene obtained with the G3 computational method.

2,2'-Bithiophene conformer	$\frac{E_{el}(G3)}{\text{hartree}}$
Syn-gauche	−1104.313528
Anti-gauche	−1104.314134

Table S29. Electronic energies (corrected for BSSE by the counterpoise method), E_{el}, used for the calculations of dimerization energies, obtained from the optimization at the B97D/6-31+G(d,p), MP2/cc-pVDZ//B97D/6-31+G(d,p) and M06-2X/6-31+G(d,p) levels of theory.

Molecular system	E_{el} / hartree		
	B97D	MP2//B97D	M06-2X
Thiophene	−552.8931814	−551.9837451	−552.9071702
Thiophene dimer A	−1105.789439	−1103.969516	---
Thiophene dimer B	−1105.789728	−1103.970106	---
Thiophene dimer C	−1105.789866	−1103.970142	---
Thiophene dimer D	−1105.788133	−1103.969333	---
Thiophene dimer E	−1105.790058	−1103.970163	---
Thiophene dimer F	−1105.791146	−1103.971581	−1105.819740
Thiophene dimer G	−1105.790743	−1103.970981	---
Thiophene dimer H	−1105.790709	−1103.970845	---
2,2'-Bithiophene	−1104.594131	−1102.806987	−1104.635105
2,2'-Bithiophene parallel dimer	−2209.199192	−2205.626251	−2209.284684
2,2'-Bithiophene antiparallel dimer	−2209.198006	−2205.62356	−2209.283753
3,3'-Bithiophene	−1104.593809	−1102.804743	−1104.634743
3,3'-Bithiophene parallel dimer	−2209.199960	−2205.623177	−2209.285318
3,3'-Bithiophene antiparallel dimer	−2209.198738	−2205.620666	−2209.283504

2,2’;5’,2’’-Terthiophene	−1656.296336	−1653.631579	−1656.363640
2,2’;5’,2’’-Terthiophene parallel dimer	−3312.608352	−3307.280853	−3312.746335
2,2’;5’,2’’-Terthiophene antiparallel dimer	−3312.607654	−3307.279939	−3312.746046
3,2’;5’,3’’-Terthiophene	−1656.294509	−1653.629663	−1656.362690
3,2’;5’,3’’-Terthiophene parallel dimer	−3312.605186	−3307.275077	−3312.743923
3,2’;5’,3’’-Terthiophene antiparallel dimer	−3312.607654	−3307.279929	−3312.746038
α-Quaterthiophene	−2207.998808	−2204.456301	−2208.092218
α-Quaterthiophene parallel dimer	−4416.019219	−4408.937509	−4416.208641
α-Quaterthiophene antiparallel dimer	−4416.018258	−4408.937203	−4416.210133

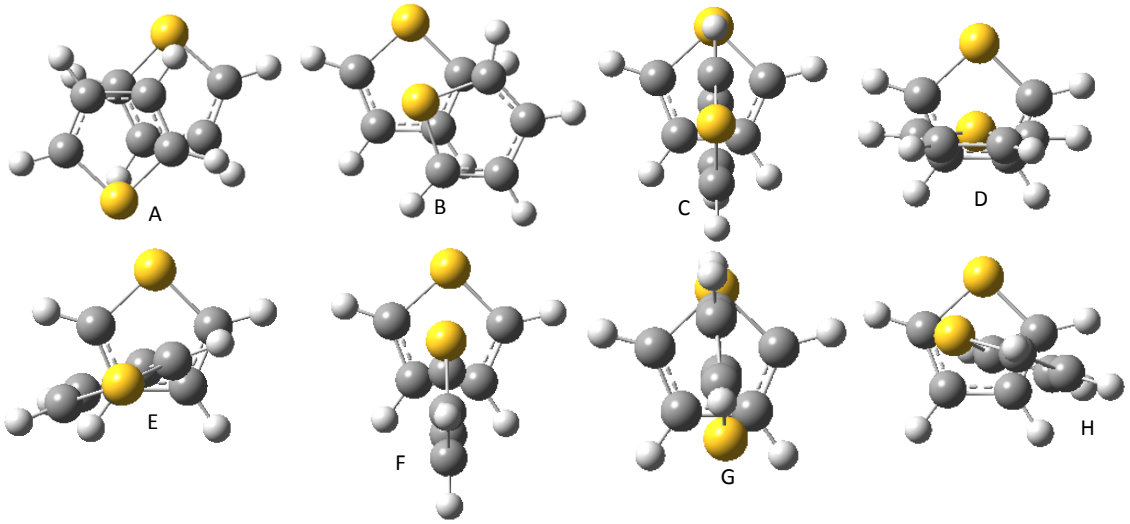

Figure S27. Graphical representation of the different dimers of thiophene optimized at the B97D/6-31+G(d,p) level of theory.

Table S30. Interaction energies, $\Delta_{int}E_m$, (corrected for BSSE) calculated at the B97D/6-31+G(d,p) level of theory using the PCM method for the parallel and anti-parallel dimers of thiophene, the bithiophenes, the terthiophenes and α-quaterthiophene in acetone and chloroform solutions.

		$\Delta_{int}E_m$ / kJ·mol^{-1}	
Dimer		acetone	chloroform
thiophene	[a]	−12.4	−12.7
22-BT / 22-BT	parallel	−28.7	−30.3
	anti-parallel	−27.5	−28.4
33-BT / 33-BT	parallel	−28.6	−31.5
	anti-parallel	−28.6	−30.1
2252-TT / 2252-TT	parallel	−44.6	−45.9
	anti-parallel	−42.9	−44.1
3253-TT / 3253-TT	parallel	−44.1	−45.7
	anti-parallel	−49.0	−51.2
α-quaterthiophene	parallel	−61.7	−63.2
	anti-parallel	−60.3	−61.6

[a] For thiophene $\Delta_{int}E_m$ for the strongest interacting dimer is shown.

Table S31. Electronic energies used for the calculations of dimerization energies, obtained from the optimization at the B97D/6-31+G(d,p) level of theory with counterpoise correction followed by a single point energy calculation at the same level of theory using the PCM method as the self-consistent reaction field.

Molecular system	$\frac{E_{el}(\text{B97D/6-31+G(d,p)/PCM(chloroform)})}{\text{hartree}}$	$\frac{E_{el}(\text{B97D/6-31+G(d,p)/PCM(acetone)})}{\text{hartree}}$
Thiophene	−552.895349	−552.8960815
Thiophene dimer F	−1105.79554	−1105.796874
2,2'-Bithiophene	−1104.597301	−1104.598495
2,2'-Bithiophene parallel dimer	−2209.206151	−2209.207911
2,2'-Bithiophene antiparallel dimer	−2209.205402	−2209.207470
3,3'-Bithiophene	−1104.597607	−1104.599067
3,3'-Bithiophene parallel dimer	−2209.207217	−2209.209032
3,3'-Bithiophene antiparallel dimer	−2209.206661	−2209.209034
2,2';5',2''-Terthiophene	−1656.300502	−1656.302092
2,2';5',2''-Terthiophene parallel dimer	−3312.618502	−3312.621167

2,2’;5’,2’’-Terthiophene antiparallel dimer	−3312.617808	−3312.620524
3,2’;5’,3’’-Terthiophene	−1656.299146	−1656.300929
3,2’;5’,3’’-Terthiophene parallel dimer	−3312.615691	−3312.618668
3,2’;5’,3’’-Terthiophene antiparallel dimer	−3312.617806	−3312.620521
α-Quaterthiophene	−2208.003989	−2208.005978
α-Quaterthiophene parallel dimer	−4416.032057	−4416.035457
α-Quaterthiophene antiparallel dimer	−4416.031445	−4416.034923

Table S32. Electronic energies used for the calculations of dimerization energies, obtained from the optimization at the B97D/6-31+G(g,p) level of theory with counterpoise correction followed by fundamental vibrational frequencies calculations at the same level of theory.

Molecular system	$\frac{E_{0\,\mathrm{K}}\,(\mathrm{B97D/6\text{-}31+G(d,p)\ +\ ZPE})}{\mathrm{hartree}}$
Thiophene	−552.8283414
Thiophene dimer F	−1105.660854
2,2’-Bithiophene	−1104.483407
2,2’-Bithiophene parallel dimer	−2208.977128
2,2’;5’,2’’-Terthiophene	−1656.139894
2,2’;5’,2’’-Terthiophene parallel dimer	−3312.294120
α-Quaterthiophene	−2207.796741
α-Quaterthiophene parallel dimer	−4415.613417

Table S33. Mean H^1-NMR chemical shifts of all protons of the different monomers and dimers calculated with the B97D/6-31+G(d,p)/GIAO computational method using TMS as a reference.

Monomer / Dimer	Mean δ_H
Thiophene	7.20
Thiophene dimer	6.61
22-BT	7.01
22-BT dimer parallel	6.45
33-BT	7.28
33-BT dimer parallel	6.56
2252-TT	6.98
2252-TT dimer parallel	6.70
3253-TT	7.19
3253-TT dimer antiparallel	6.64
α-quaterthiophene	6.95
α-quaterthiophene dimer parallel	6.64

Table S34. Cartesian coordinates of the optimized structures of thiophene dimer A using B97D/6-31+G(d,p) with counterpoise correction.

Center number	Atomic number	Atomic type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.0114540	1.0565600	-0.6227710
2	6	0	1.1297770	0.0606020	-0.9848790
3	6	0	1.5429960	-1.2336570	-0.5295100
4	6	0	2.7294120	-1.1991400	0.1732890
5	16	0	3.3564920	0.4216470	0.2830300
6	1	0	1.9474080	2.1217510	-0.8274280
7	1	0	0.2100450	0.2482170	-1.5352930
8	1	0	0.9820450	-2.1490780	-0.7102170
9	1	0	3.2711500	-2.0240630	0.6280370
10	6	0	-2.1186770	-1.0528810	0.7074020
11	6	0	-1.4234120	-0.0393980	1.3312340
12	6	0	-1.7155360	1.2508260	0.7808850
13	6	0	-2.6262470	1.1955230	-0.2532970
14	16	0	-3.1375310	-0.4396310	-0.5645590
15	1	0	-2.0866660	-2.1194860	0.9119450
16	1	0	-0.7136420	-0.2119020	2.1382480
17	1	0	-1.2650340	2.1783010	1.1307570
18	1	0	-3.0272960	2.0134010	-0.8457120

Table S35. Cartesian coordinates of the optimized structures of thiophene dimer B using B97D/6-31+G(d,p) with counterpoise correction.

Center number	Atomic number	Atomic type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.4418610	-0.7530960	-1.0489620
2	6	0	-1.1912060	0.5773040	-1.3040670
3	6	0	-1.8510800	1.4505320	-0.3794580
4	6	0	-2.5908210	0.7682520	0.5637260
5	16	0	-2.4881190	-0.9532630	0.3270110
6	1	0	-1.0600380	-1.6237610	-1.5740840
7	1	0	-0.5415350	0.9169750	-2.1083150
8	1	0	-1.7788550	2.5369040	-0.4084550
9	1	0	-3.1916170	1.1717330	1.3742560
10	6	0	2.5920950	0.7636370	-0.5669050
11	6	0	1.8554950	1.4510840	0.3749720
12	6	0	1.1941080	0.5827770	1.3031720
13	6	0	1.4403550	-0.7491410	1.0519370
14	16	0	2.4846420	-0.9567830	-0.3245260
15	1	0	3.1941170	1.1632420	-1.3784560
16	1	0	1.7864950	2.5377500	0.4001030
17	1	0	0.5468810	0.9267620	2.1075670
18	1	0	1.0576720	-1.6169680	1.5811310

Table S36. Cartesian coordinates of the optimized structures of thiophene dimer C using B97D/6-31+G(d,p) with counterpoise correction.

Center number	Atomic number	Atomic type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.5626790	0.0255890	1.2497370
2	6	0	2.3561690	1.2876750	0.7336870
3	6	0	2.3592950	1.3062690	-0.7001450
4	6	0	2.5680020	0.0579550	-1.2479170
5	16	0	2.7678050	-1.1533540	-0.0141120
6	1	0	2.6037380	-0.2801510	2.2914290
7	1	0	2.2056680	2.1680620	1.3569180
8	1	0	2.2117370	2.2025820	-1.3009970
9	1	0	2.6139570	-0.2207470	-2.2969630
10	6	0	-2.4723560	-1.2786350	0.0037060
11	6	0	-1.2397800	-0.6594790	0.0016310
12	6	0	-1.3400760	0.7706700	-0.0035770
13	6	0	-2.6465650	1.2129350	-0.0054470
14	16	0	-3.7701650	-0.1174850	-0.0006750
15	1	0	-2.6953540	-2.3421650	0.0075180
16	1	0	-0.2946180	-1.1993170	0.0036810
17	1	0	-0.4761830	1.4321850	-0.0057860
18	1	0	-3.0153910	2.2351050	-0.0092740

Table S37. Cartesian coordinates of the optimized structures of thiophene dimer D using B97D/6-31+G(d,p) with counterpoise correction.

Center number	Atomic number	Atomic type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-2.4512930	1.2504560	-0.0109620
2	6	0	-2.3172880	0.7404180	1.2639650
3	6	0	-2.3268790	-0.6923840	1.2892980
4	6	0	-2.4681200	-1.2452740	0.0331980
5	16	0	-2.5909380	-0.0178530	-1.1932610
6	1	0	-2.4778360	2.2907890	-0.3232630
7	1	0	-2.2128150	1.3662640	2.1491980
8	1	0	-2.2300470	-1.2879310	2.1959850
9	1	0	-2.5079510	-2.2955830	-0.2422780
10	6	0	2.4507430	1.2442150	-0.0078420
11	6	0	3.7269430	0.7320390	-0.1270170
12	6	0	3.7474750	-0.7012620	-0.1224800
13	6	0	2.4863960	-1.2489150	-0.0002610
14	16	0	1.2611590	-0.0191610	0.1112180
15	1	0	2.1414030	2.2856430	0.0152810
16	1	0	4.6153330	1.3562050	-0.2147510
17	1	0	4.6533760	-1.3003200	-0.2061130
18	1	0	2.2071230	-2.2986070	0.0312380

Table S38. Cartesian coordinates of the optimized structures of thiophene dimer E using B97D/6-31+G(d,p) with counterpoise correction.

Center number	Atomic number	Atomic type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.5073830	-1.2411880	0.1375060
2	6	0	2.3246050	-0.5916700	1.3411290
3	6	0	2.3625250	0.8349220	1.2092400
4	6	0	2.5728740	1.2427890	-0.0922150
5	16	0	2.7252290	-0.1144330	-1.1694650
6	1	0	2.5295270	-2.3100960	-0.0566840
7	1	0	2.1675310	-1.1139880	2.2836650
8	1	0	2.2385300	1.5286500	2.0395110
9	1	0	2.6480150	2.2552250	-0.4794970
10	6	0	-2.5691310	-1.2481130	0.0252640
11	6	0	-1.2867310	-0.7501140	0.1247330
12	6	0	-1.2437980	0.6823140	0.0795520
13	6	0	-2.4950340	1.2474040	-0.0533280
14	16	0	-3.7403280	0.0320530	-0.1245930
15	1	0	-2.8954180	-2.2846310	0.0301860
16	1	0	-0.4003390	-1.3733920	0.2267100
17	1	0	-0.3226170	1.2586570	0.1438340
18	1	0	-2.7598070	2.2995960	-0.1140840

Table S39. Cartesian coordinates of the optimized structures of thiophene dimer F using B97D/6-31+G(d,p) with counterpoise correction.

Center number	Atomic number	Atomic type	Coordinates (Angstroms)		
			X	Y	Z
1	16	0	-2.4883920	0.2563170	-1.1577380
2	6	0	-2.6447260	1.1198280	0.3449040
3	6	0	-1.9568820	-1.1808880	-0.3351460
4	6	0	-2.3043340	0.3264950	1.4219820
5	1	0	-2.9807800	2.1530890	0.3467930
6	6	0	-1.9088890	-0.9947380	1.0309790
7	1	0	-1.7036640	-2.0706890	-0.9044210
8	1	0	-2.3313870	0.6762950	2.4528920
9	1	0	-1.5933150	-1.7697970	1.7274780
10	1	0	0.1587560	0.8201670	0.3548590
11	6	0	1.2115090	0.6099110	0.1911950
12	6	0	2.2674170	1.4922520	0.0972160
13	16	0	1.7451130	-1.0367810	0.0154260
14	6	0	3.5242540	0.8356310	-0.1190040
15	1	0	2.1486310	2.5719650	0.1795960
16	6	0	3.4011560	-0.5369480	-0.1852570
17	1	0	4.4763830	1.3549860	-0.2211050
18	1	0	4.1808150	-1.2778580	-0.3402980

Table S40. Cartesian coordinates of the optimized structures of thiophene dimer G using B97D/6-31+G(d,p) with counterpoise correction.

Center number	Atomic number	Atomic type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.4023030	-0.0547750	1.2523230
2	6	0	2.3540050	1.2474760	0.7995120
3	6	0	2.3770000	1.3358450	-0.6315870
4	6	0	2.4422560	0.0988690	-1.2394410
5	16	0	2.4797050	-1.1861030	-0.0671110
6	1	0	2.3907130	-0.4141210	2.2774710
7	1	0	2.2988810	2.1077200	1.4649100
8	1	0	2.3428160	2.2715560	-1.1876250
9	1	0	2.4662060	-0.1319180	-2.3007580
10	6	0	-3.6720050	-0.0815170	0.0116260
11	6	0	-3.0791270	-1.3273350	0.0230520
12	6	0	-1.6467680	-1.2583450	0.0028550
13	6	0	-1.1742440	0.0370650	-0.0235110
14	16	0	-2.4801540	1.1873880	-0.0238530
15	1	0	-4.7304490	0.1639420	0.0217470
16	1	0	-3.6468390	-2.2567990	0.0450340
17	1	0	-0.9899590	-2.1268800	0.0074200
18	1	0	-0.1447100	0.3822310	-0.0417470

Table S41. Cartesian coordinates of the optimized structures of thiophene dimer H using B97D/6-31+G(d,p) with counterpoise correction.

Center number	Atomic number	Atomic type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.4808580	-1.1106470	0.5007660
2	6	0	2.3848660	-0.0989150	1.4349090
3	6	0	2.2925970	1.1995100	0.8340240
4	6	0	2.3208750	1.1495930	-0.5445210
5	16	0	2.4625570	-0.4843480	-1.1221020
6	1	0	2.5637340	-2.1806670	0.6703990
7	1	0	2.3762200	-0.2777180	2.5090510
8	1	0	2.2040740	2.1279370	1.3961870
9	1	0	2.2610970	1.9722600	-1.2516150
10	6	0	-3.6266960	-0.1097040	-0.2051520
11	6	0	-3.1831700	1.1962170	-0.2438340
12	6	0	-1.7788500	1.3108790	0.0237260
13	6	0	-1.1782780	0.0923800	0.2617170
14	16	0	-2.3275710	-1.2100210	0.1598340
15	1	0	-4.6323690	-0.4873590	-0.3684310
16	1	0	-3.8370300	2.0412690	-0.4560910
17	1	0	-1.2322240	2.2526870	0.0388450
18	1	0	-0.1364940	-0.1143700	0.4881180

Table S42. Cartesian coordinates of the optimized structures of 2,2'-bithiophene parallel dimer using B97D/6-31+G(d,p) with counterpoise correction.

Center number	Atomic number	Atomic type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.4015390	0.3773280	-3.0073990
2	6	0	-1.3268160	0.8662270	-1.6680810
3	1	0	-1.1034060	0.9532490	-3.8822540
4	6	0	-1.8733510	-0.9185280	-3.0801310
5	6	0	-1.7373480	-0.0618350	-0.7230270
6	1	0	-0.9313710	1.8407060	-1.3879390
7	1	0	-2.0283230	-1.5312100	-3.9642480
8	16	0	-2.2512290	-1.5509600	-1.5048410
9	6	0	-1.7362870	0.0610350	0.7254360
10	6	0	-1.3240820	-0.8668030	1.6699830
11	16	0	-2.2494150	1.5501120	1.5078670
12	6	0	-1.3968300	-0.3777030	3.0093480
13	1	0	-0.9290690	-1.8413290	1.3894490
14	6	0	-1.8688480	0.9180560	3.0826210
15	1	0	-1.0973190	-0.9534120	3.8838640
16	1	0	-2.0228060	1.5307460	3.9669200
17	1	0	2.0238150	3.9659350	-1.5323470
18	6	0	1.8696980	3.0816970	-0.9196210
19	6	0	1.3987890	3.0086590	0.3765430
20	16	0	2.2487630	1.5067200	-1.5520980
21	6	0	1.3257050	1.6693290	0.8656350
22	1	0	1.1002690	3.8833200	0.9525540
23	6	0	1.7366670	0.7245800	-0.0625250
24	1	0	0.9312740	1.3889340	1.8404280
25	6	0	1.7368760	-0.7238880	0.0603660

26	6	0	1.3247620	-1.6687340	-0.8671890
27	16	0	2.2521210	-1.5059890	1.5488830
28	6	0	1.3993330	-3.0081050	-0.3784060
29	1	0	0.9285580	-1.3883720	-1.8412690
30	6	0	1.8726690	-3.0810820	0.9168770
31	1	0	1.1001480	-3.8828060	-0.9540180
32	1	0	2.0280110	-3.9653060	1.5293170

Table S43. Cartesian coordinates of the optimized structures of 2,2'-bithiophene antiparallel dimer using B97D/6-31+G(d,p) with counterpoise correction.

Center number	Atomic number	Atomic type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-3.0483340	-1.7079140	-0.2319680
2	6	0	-1.8532950	-1.6901400	0.5441480
3	1	0	-4.0488040	-1.6735360	0.1957320
4	6	0	-2.8059640	-1.7574390	-1.5884650
5	6	0	-0.6927530	-1.7268120	-0.2189620
6	1	0	-1.8389520	-1.6308230	1.6306480
7	16	0	-1.1005350	-1.7853050	-1.9323140
8	1	0	-3.5221260	-1.7781890	-2.4052990
9	6	0	0.6904190	-1.7275200	0.2192240
10	6	0	1.8509920	-1.6929510	-0.5439380
11	16	0	1.0982020	-1.7849490	1.9326610
12	6	0	3.0460310	-1.7113150	0.2321560
13	1	0	1.8366930	-1.6346450	-1.6305010
14	6	0	2.8036410	-1.7592750	1.5887010
15	1	0	4.0465250	-1.6784110	-0.1956050
16	1	0	3.5198090	-1.7800180	2.4055260
17	6	0	-0.6904180	1.7272370	0.2189940
18	6	0	-1.8509980	1.6924160	-0.5441500
19	6	0	0.6927470	1.7264970	-0.2192150
20	16	0	-1.0981500	1.7855570	1.9323530
21	6	0	-3.0460200	1.7114200	0.2319550
22	1	0	-1.8367200	1.6335550	-1.6306800
23	6	0	1.8533080	1.6898310	0.5438660
24	16	0	1.1004810	1.7851080	-1.9325850
25	6	0	-2.8036040	1.7600340	1.5884670
26	1	0	-4.0465330	1.6785180	-0.1957630
27	6	0	3.0483290	1.7076560	-0.2322780
28	1	0	1.8390030	1.6304900	1.6303640
29	6	0	2.8059230	1.7572460	-1.5887610
30	1	0	-3.5197480	1.7813310	2.4053020
31	1	0	4.0488110	1.6732780	0.1953970
32	1	0	3.5220580	1.7780620	-2.4056180

Table S44. Cartesian coordinates of the optimized structures of 3,3'-bithiophene parallel dimer using B97D/6-31+G(d,p) with counterpoise correction.

Center number	Atomic number	Atomic type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.2646500	2.7588310	1.8998960
2	6	0	-0.1804230	1.9202320	2.0093080
3	6	0	-0.4890870	0.5491050	1.6949930
4	6	0	-1.8215300	0.3891940	1.3546600
5	16	0	-2.6931710	1.8895710	1.4063420
6	1	0	-1.3163490	3.8254220	2.1005450
7	1	0	0.8096830	2.2534090	2.3149430
8	1	0	-2.3115190	-0.5151400	1.0080450
9	6	0	0.4914430	-0.5463260	1.6952240
10	6	0	1.8234520	-0.3868830	1.3529520
11	6	0	0.1832650	-1.9169470	2.0121880
12	16	0	2.6952690	-1.8870980	1.4061140
13	1	0	2.3129460	0.5169270	1.0042640
14	6	0	1.2674230	-2.7556520	1.9028260
15	1	0	-0.8064260	-2.2497050	2.3196240
16	1	0	1.3194240	-3.8219150	2.1051340
17	6	0	2.7563220	1.2635270	-1.9039330
18	6	0	1.9171770	0.1796180	-2.0123030
19	6	0	0.5466490	0.4886820	-1.6957920
20	6	0	0.3877240	1.8211090	-1.3549150
21	16	0	1.8883080	2.6922480	-1.4087840
22	1	0	3.8226260	1.3148870	-2.1061830
23	1	0	2.2495620	-0.8105260	-2.3186760
24	1	0	-0.5159080	2.3113260	-1.0067890
25	6	0	-0.5491330	-0.4914470	-1.6944970
26	6	0	-0.3895920	-1.8236910	-1.3531850
27	6	0	-1.9202330	-0.1825740	-2.0087130
28	16	0	-1.8902520	-2.6948820	-1.4039020
29	1	0	0.5147190	-2.3137430	-1.0066000
30	6	0	-2.7591730	-1.2664280	-1.8982350
31	1	0	-2.2531820	0.8074130	-2.3149720
32	1	0	-3.8258490	-1.3178980	-2.0984870

Table S45. Cartesian coordinates of the optimized structures of 3,3'-bithiophene antiparallel dimer using B97D/6-31+G(d,p) with counterpoise correction.

Center number	Atomic number	Atomic type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-3.0057720	1.7294270	0.4482840
2	6	0	-1.9116160	1.7518520	-0.3807060
3	6	0	-0.6586340	1.6521890	0.3228180
4	6	0	-0.8559210	1.5536900	1.6917350
5	16	0	-2.5377920	1.5850710	2.1191080
6	1	0	-4.0563050	1.7843490	0.1779710
7	1	0	-1.9900240	1.8317030	-1.4625000
8	1	0	-0.1009910	1.4518330	2.4645570
9	6	0	0.6597920	1.6517320	-0.3235490
10	6	0	0.8570480	1.5523800	-1.6924110
11	6	0	1.9128090	1.7513060	0.3799230
12	16	0	2.5389340	1.5828860	-2.1197940
13	1	0	0.1020820	1.4504070	-2.4651830
14	6	0	3.0069600	1.7279990	-0.4490500
15	1	0	1.9912380	1.8317280	1.4616730
16	1	0	4.0575120	1.7826730	-0.1787620
17	6	0	-3.0069640	-1.7282060	-0.4483190
18	6	0	-1.9128290	-1.7512810	0.3806790
19	6	0	-0.6597940	-1.6521240	-0.3228170
20	6	0	-0.8570150	-1.5533610	-1.6917270
21	16	0	-2.5389000	-1.5838650	-2.1191220
22	1	0	-4.0575260	-1.7826490	-0.1780230
23	1	0	-1.9912800	-1.8312510	1.4624620
24	1	0	-0.1020300	-1.4517570	-2.4645280
25	6	0	0.6586200	-1.6522200	0.3235660
26	6	0	0.8558920	-1.5530120	1.6924340
27	6	0	1.9116130	-1.7520300	-0.3799140
28	16	0	2.5377780	-1.5838540	2.1198090
29	1	0	0.1009530	-1.4508920	2.4652130
30	6	0	3.0057680	-1.7289640	0.4490530
31	1	0	1.9900210	-1.8324250	-1.4616670
32	1	0	4.0563080	-1.7837980	0.1787530

Table S46. Cartesian coordinates of the optimized structures of 2,2';5',2''-terthiophene parallel dimer using B97D/6-31+G(d,p) with counterpoise correction.

Center number	Atomic number	Atomic type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	4.9573350	-2.7773610	-0.8285630
2	6	0	4.0459970	-2.9762480	-1.8463930
3	6	0	2.7121180	-2.6353620	-1.4702940
4	6	0	2.6063580	-2.1742910	-0.1617740
5	16	0	4.1867590	-2.1875480	0.6156340
6	1	0	6.0306920	-2.9461280	-0.8404870
7	1	0	4.3248770	-3.3423840	-2.8334560
8	1	0	1.8540020	-2.6908090	-2.1383530
9	6	0	1.4335800	-1.7021950	0.5451950
10	6	0	1.3505540	-0.7357770	1.5396770
11	16	0	-0.1704850	-2.3087880	0.1454680
12	6	0	0.0234970	-0.4587200	1.9514300
13	1	0	2.2245640	-0.1995090	1.9031340
14	6	0	-0.9412680	-1.2077950	1.2854920
15	1	0	-0.2319670	0.3027490	2.6853000
16	6	0	-2.3807820	-1.1683330	1.4277950
17	6	0	-3.3559690	-1.7725780	0.6422090
18	16	0	-3.1394180	-0.2529210	2.7305230
19	6	0	-4.6862870	-1.5050040	1.0763010
20	1	0	-3.1149090	-2.3626780	-0.2389780
21	6	0	-4.7336770	-0.6952230	2.1919990
22	1	0	-5.5746320	-1.8839060	0.5742270
23	1	0	-5.6052290	-0.3271290	2.7260930
24	6	0	4.7010960	2.8811010	0.5314380
25	6	0	4.6531820	1.7242250	-0.2194860
26	6	0	3.3246290	1.3445450	-0.5716250
27	6	0	2.3536300	2.2167640	-0.0898480
28	16	0	3.1104140	3.5340770	0.8053120
29	1	0	5.5710480	3.3899880	0.9374170
30	1	0	5.5381130	1.1541590	-0.4970470
31	1	0	3.0778720	0.4389460	-1.1225880
32	6	0	0.9149100	2.1313170	-0.2221170
33	6	0	-0.0803380	2.7271290	0.5478230
34	16	0	0.1955170	1.1264170	-1.4701760
35	6	0	-1.3940070	2.3553270	0.1665190
36	1	0	0.1447410	3.3787350	1.3908710
37	6	0	-1.4342190	1.4680490	-0.9050470
38	1	0	-2.2919320	2.6849860	0.6861860
39	6	0	-2.5771580	0.8398360	-1.5308080
40	6	0	-2.6096560	-0.2536130	-2.3913890
41	16	0	-4.2109140	1.4229580	-1.2327890
42	6	0	-3.9267830	-0.6207860	-2.7938920
43	1	0	-1.7090340	-0.7855060	-2.6933550
44	6	0	-4.9002580	0.1881570	-2.2427720
45	1	0	-4.1496380	-1.4537320	-3.4593460
46	1	0	-5.9774440	0.1361040	-2.3743940

Table S47. Cartesian coordinates of the optimized structures of 2,2';5',2''-terthiophene antiparallel dimer using B97D/6-31+G(d,p) with counterpoise correction.

Center number	Atomic number	Atomic type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.0521520	-2.4580100	1.1587960
2	6	0	1.3586250	-2.3095200	1.1738820
3	1	0	-0.6324040	-2.8233350	2.0048610
4	6	0	-0.6442430	-2.0501250	-0.0329750
5	6	0	1.8793470	-1.7869520	-0.0065880
6	1	0	1.9842350	-2.5525370	2.0317270
7	16	0	0.5857890	-1.5006430	-1.1636720
8	6	0	-2.0442880	-2.0350680	-0.4011910
9	6	0	3.2538530	-1.4841210	-0.3446050
10	6	0	-2.6759640	-1.3048100	-1.4009090
11	16	0	-3.2218970	-3.0232090	0.4615740
12	6	0	3.7450060	-0.6617240	-1.3517360
13	16	0	4.5883530	-2.1798570	0.5726890
14	6	0	-4.0818570	-1.5263810	-1.4662110
15	1	0	-2.1407650	-0.5955040	-2.0289320
16	6	0	-4.5277640	-2.4235000	-0.5190490
17	6	0	5.1677390	-0.5846610	-1.3803200
18	1	0	3.0918640	-0.1034750	-2.0194840
19	6	0	5.7672580	-1.3453850	-0.3981330
20	1	0	-4.7439320	-1.0201720	-2.1659910
21	1	0	-5.5435900	-2.7592340	-0.3310690
22	1	0	5.7277490	0.0213570	-2.0906420
23	1	0	6.8259390	-1.4669500	-0.1863810
24	1	0	2.1411700	0.5957540	2.0289100
25	6	0	2.6761930	1.3049990	1.4006740
26	6	0	2.0443540	2.0348380	0.4007490
27	6	0	4.0820250	1.5269560	1.4659810
28	6	0	0.6442580	2.0498470	0.0327280
29	16	0	3.2217770	3.0229830	-0.4622880
30	6	0	4.5277480	2.4239050	0.5185720
31	1	0	4.7441840	1.0212010	2.1660120
32	6	0	0.0519350	2.4582250	-1.1587670
33	16	0	-0.5856070	1.5001240	1.1635070
34	1	0	5.5434980	2.7598370	0.3305270
35	6	0	-1.3588620	2.3099510	-1.1735810
36	1	0	0.6320250	2.8238280	-2.0048240
37	6	0	-1.8793980	1.7870780	0.0068370
38	1	0	-1.9846280	2.5533680	-2.0311990
39	6	0	-3.2538680	1.4842310	0.3449980
40	6	0	-3.7448900	0.6615770	1.3519850
41	16	0	-4.5884950	2.1800830	-0.5720340
42	6	0	-5.1676130	0.5843690	1.3806330
43	1	0	-3.0916550	0.1032380	2.0195680
44	6	0	-5.7672630	1.3452750	0.3986680
45	1	0	-5.7275200	-0.0218730	2.0908440
46	1	0	-6.8259690	1.4668370	0.1870430

Table S48. Cartesian coordinates of the optimized structures of 3,2';5',3''-terthiophene parallel dimer using B97D/6-31+G(d,p) with counterpoise correction.

Center number	Atomic number	Atomic type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.4081270	-0.4913470	1.6514000
2	6	0	-0.0970310	-0.1035080	2.0250740
3	1	0	-2.3031240	0.0632350	1.9241890
4	6	0	-1.4471690	-1.6106280	0.8309040
5	6	0	0.9012980	-0.9133800	1.5006580
6	1	0	0.1204040	0.7746390	2.6280940
7	16	0	0.1831310	-2.2000290	0.5411870
8	6	0	-2.6148980	-2.2453640	0.2276580
9	6	0	2.3462520	-0.7766270	1.6489070
10	6	0	-3.9177770	-2.0300540	0.6634350
11	6	0	-2.5840190	-3.1332770	-0.9104700
12	6	0	2.9475610	0.2026360	2.4305510
13	6	0	3.3324530	-1.6035600	0.9973850
14	16	0	-5.0818910	-2.8821730	-0.2981950
15	1	0	-4.2414730	-1.4256020	1.5047350
16	6	0	-3.8314980	-3.5554430	-1.3048280
17	1	0	-1.6673160	-3.4271410	-1.4194120
18	16	0	4.6775900	0.1190920	2.3720540
19	1	0	2.4588500	0.9610270	3.0336010
20	6	0	4.6244630	-1.2441930	1.2914570
21	1	0	3.0849840	-2.4182800	0.3203850
22	1	0	-4.0893100	-4.2127070	-2.1304800
23	1	0	5.5451520	-1.6857660	0.9226530
24	1	0	-3.0349530	0.3755380	-0.8265350
25	6	0	-3.2932440	1.3788280	-0.4946650
26	6	0	-2.3183750	2.4059800	-0.2149710
27	6	0	-4.5847800	1.7784200	-0.2468110
28	6	0	-2.9233560	3.5718760	0.2390170
29	6	0	-0.8735790	2.2420140	-0.3505110
30	16	0	-4.6489110	3.4187550	0.3351460
31	1	0	-5.4979320	1.2008670	-0.3602340
32	1	0	-2.4419390	4.5120990	0.4909090
33	6	0	0.1413530	2.9025020	0.3310110
34	16	0	-0.1902270	1.0638620	-1.4521320
35	6	0	1.4439190	2.4515770	-0.0101570
36	1	0	-0.0637040	3.6541320	1.0920780
37	6	0	1.4514100	1.4383030	-0.9601600
38	1	0	2.3561730	2.8148330	0.4592620
39	6	0	2.5955580	0.7236430	-1.5168770
40	6	0	3.9089530	1.1608840	-1.4001500
41	6	0	2.5208800	-0.5233190	-2.2393900
42	16	0	5.0311960	0.0738740	-2.1464890
43	1	0	4.2654420	2.0653910	-0.9178650
44	6	0	3.7484240	-0.9915470	-2.6425310
45	1	0	1.5885440	-1.0521080	-2.4293890
46	1	0	3.9739800	-1.9007470	-3.1927440

Table S49. Cartesian coordinates of the optimized structures of 3,2';5',3''-terthiophene antiparallel dimer using B97D/6-31+G(d,p) with counterpoise correction.

Center number	Atomic number	Atomic type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.0507320	2.4598260	1.1574320
2	6	0	-1.3600570	2.3115830	1.1730600
3	1	0	0.6312360	2.8263350	2.0028130
4	6	0	0.6425100	2.0501110	-0.0338740
5	6	0	-1.8811310	1.7874250	-0.0065560
6	1	0	-1.9854340	2.5559050	2.0307030
7	16	0	-0.5878830	1.4992500	-1.1635310
8	6	0	2.0424480	2.0346840	-0.4024840
9	6	0	-3.2557330	1.4840060	-0.3436580
10	6	0	2.6739370	1.3034610	-1.4016070
11	16	0	3.2201480	3.0242340	0.4585990
12	6	0	-3.7471560	0.6602690	-1.3495490
13	16	0	-4.5899820	2.1801670	0.5737300
14	6	0	4.0797320	1.5254090	-1.4677890
15	1	0	2.1387140	0.5932690	-2.0286040
16	6	0	4.5257740	2.4237370	-0.5218380
17	6	0	-5.1698660	0.5824680	-1.3770980
18	1	0	-3.0941860	0.1014000	-2.0169420
19	6	0	-5.7691170	1.3439490	-0.3953440
20	1	0	4.7416560	1.0186210	-2.1672920
21	1	0	5.5415980	2.7599080	-0.3346160
22	1	0	-5.7300060	-0.0246760	-2.0863520
23	1	0	-6.8277210	1.4653350	-0.1831000
24	1	0	-5.5414960	-2.7614100	0.3272940
25	6	0	-4.5258590	-2.4255950	0.5161480
26	6	0	-4.0807930	-1.5288680	1.4640640
27	16	0	-3.2192230	-3.0244740	-0.4639510
28	6	0	-2.6749230	-1.3068790	1.3997550
29	1	0	-4.7434740	-1.0230930	2.1635810
30	6	0	-2.0423960	-2.0364240	0.4000470
31	1	0	-2.1402660	-0.5979960	2.0287250
32	6	0	-0.6421110	-2.0509680	0.0327540
33	6	0	-0.0490270	-2.4596050	-1.1582750
34	16	0	0.5869030	-1.4997780	1.1637320
35	6	0	1.3616770	-2.3104440	-1.1725650
36	1	0	-0.6285230	-2.8260450	-2.0043770
37	6	0	1.8813760	-1.7865440	0.0077660
38	1	0	1.9879730	-2.5539810	-2.0297630
39	6	0	3.2554920	-1.4826210	0.3463330
40	6	0	3.7456130	-0.6594850	1.3533670
41	16	0	4.5909080	-2.1776620	-0.5701700
42	6	0	5.1682780	-0.5813300	1.3825020
43	1	0	3.0917860	-0.1015700	2.0207270
44	6	0	5.7687760	-1.3418950	0.4007920
45	1	0	5.7275300	0.0253350	2.0928710
46	1	0	6.8276350	-1.4627180	0.1895080

Table S50. Cartesian coordinates of the optimized structures of α-quaterthiophene parallel dimer using B97D/6-31+G(d,p) with counterpoise correction.

Center number	Atomic number	Atomic type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	7.5559820	1.7645370	-0.2699960
2	6	0	7.0766780	2.3141020	0.9022310
3	16	0	6.2636840	1.2776280	-1.3250780
4	1	0	8.5881060	1.6194500	-0.5766430
5	6	0	5.6524640	2.3350880	0.9611780
6	1	0	7.7238510	2.6851790	1.6957780
7	6	0	5.0420130	1.7994910	-0.1698620
8	1	0	5.0838770	2.7109060	1.8106780
9	6	0	3.6330840	1.6363860	-0.4537320
10	6	0	3.0194780	0.8346230	-1.4108570
11	16	0	2.4161100	2.5057980	0.4789670
12	6	0	1.6054400	0.8988230	-1.3907640
13	1	0	3.5842050	0.1825020	-2.0736860
14	6	0	1.0963590	1.7476480	-0.4117000
15	1	0	0.9653820	0.2956800	-2.0307460
16	6	0	-0.2790740	2.0245140	-0.0747250
17	6	0	-0.7992170	2.6185680	1.0741440
18	16	0	-1.5838480	1.5954800	-1.1765980
19	6	0	-2.2137930	2.6995200	1.0833830
20	1	0	-0.1677730	2.9536970	1.8958170
21	6	0	-2.8123940	2.1697860	-0.0567250
22	1	0	-2.7928900	3.1022020	1.9131860
23	6	0	-4.2182650	2.0459330	-0.3753660
24	6	0	-4.8342470	1.1944450	-1.2857390
25	16	0	-5.4273030	3.0370580	0.4401580
26	6	0	-6.2520870	1.3288000	-1.3220630
27	1	0	-4.2775250	0.4670030	-1.8722040
28	6	0	-6.7228190	2.2805830	-0.4417140
29	1	0	-6.9015490	0.7212670	-1.9486790
30	1	0	-7.7506460	2.5764990	-0.2508590
31	1	0	-0.9637190	-0.2950910	2.0303260
32	6	0	-1.6044300	-0.8982530	1.3910190
33	6	0	-1.0962300	-1.7475190	0.4118840
34	6	0	-3.0184570	-0.8334910	1.4118880
35	6	0	0.2789250	-2.0247150	0.0740660
36	16	0	-2.4166930	-2.5053760	-0.4778440
37	6	0	-3.6328690	-1.6352580	0.4552630
38	1	0	-3.5825530	-0.1812710	2.0751700
39	16	0	1.5843050	-1.5965650	1.1755020
40	6	0	0.7983560	-2.6181330	-1.0754510
41	6	0	-5.0419270	-1.7985060	0.1720990
42	6	0	2.8122170	-2.1701030	0.0545240
43	6	0	2.2129450	-2.6991280	-1.0855580
44	1	0	0.1663930	-2.9527790	-1.8969210
45	6	0	-5.6526370	-2.3354990	-0.9581520
46	16	0	-6.2633340	-1.2759950	1.3272740
47	6	0	4.2181850	-2.0463800	0.3728140
48	1	0	2.7915170	-3.1011870	-1.9160330
49	6	0	-7.0768220	-2.3152240	-0.8985860
50	1	0	-5.0842330	-2.7119600	-1.8074910
51	6	0	-7.5558760	-1.7647330	0.2733120

52	6	0	4.8340440	-1.1960300	1.2843450
53	16	0	5.4273040	-3.0367190	-0.4434980
54	1	0	-7.7241560	-2.6876580	-1.6913640
55	1	0	-8.5879290	-1.6198730	0.5803030
56	6	0	6.2518140	-1.3308070	1.3211650
57	1	0	4.2772450	-0.4687980	1.8709870
58	6	0	6.7226830	-2.2815460	0.4397470
59	1	0	6.9011520	-0.7243150	1.9489170
60	1	0	7.7505050	-2.5775020	0.2489280

Table S51. Cartesian coordinates of the optimized structures of α-quaterthiophene antiparallel dimer using B97D/6-31+G(d,p) with counterpoise correction.

Center number	Atomic number	Atomic type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.6949120	2.4293740	-1.0558280
2	6	0	3.1109310	2.3795050	-1.0377640
3	1	0	1.1133320	2.8094030	-1.8944270
4	6	0	1.1008120	1.9054230	0.0913630
5	6	0	3.6379660	1.8194820	0.1232590
6	1	0	3.7397720	2.7205130	-1.8590810
7	16	0	2.3395740	1.3683720	1.2218620
8	6	0	-0.2997650	1.7680120	0.4089650
9	6	0	5.0215280	1.5980620	0.4836030
10	6	0	-0.9010920	1.0113780	1.4109500
11	16	0	-1.5310440	2.6031730	-0.5380620
12	6	0	5.5490310	0.7370240	1.4390580
13	16	0	6.3205850	2.4720180	-0.3262590
14	6	0	-2.3150900	1.0764270	1.4057210
15	1	0	-0.3272950	0.3861430	2.0921000
16	6	0	-2.8368970	1.8800580	0.3977030
17	6	0	6.9715700	0.7716460	1.5123490
18	1	0	4.9245220	0.0752230	2.0356840
19	6	0	7.5348830	1.6568280	0.6166500
20	1	0	-2.9483410	0.5078820	2.0835700
21	6	0	-4.2203820	2.1291180	0.0569950
22	1	0	7.5586060	0.1549630	2.1908760
23	1	0	8.5858140	1.8783950	0.4527650
24	6	0	-4.7532090	2.6437300	-1.1223610
25	16	0	-5.5146710	1.7600720	1.1927190
26	6	0	-6.1758010	2.7340480	-1.1118160
27	1	0	-4.1313050	2.9285360	-1.9699340
28	6	0	-6.7311210	2.2875940	0.0703470
29	1	0	-6.7680310	3.1020930	-1.9482680
30	1	0	-7.7802870	2.2277630	0.3453090
31	1	0	4.2032930	-0.4043200	-2.0631680
32	6	0	4.7950530	-1.1037170	-1.4762020
33	6	0	4.2240910	-1.9455980	-0.5286850
34	6	0	6.2144920	-1.2021600	-1.5433370
35	6	0	2.8310670	-2.0913890	-0.1669980
36	16	0	5.4778450	-2.8851360	0.2795260

37	6	0	6.7314870	-2.1168860	-0.6504280
38	1	0	6.8337790	-0.6005820	-2.2058560
39	6	0	2.2742520	-2.6171260	0.9960440
40	16	0	1.5609650	-1.5576830	-1.2609380
41	1	0	7.7712120	-2.3793700	-0.4770300
42	6	0	0.8582770	-2.5690050	1.0219540
43	1	0	2.8830150	-2.9944010	1.8164410
44	6	0	0.2945930	-2.0068880	-0.1225670
45	1	0	0.2565420	-2.9094070	1.8635120
46	6	0	-1.0940950	-1.7645860	-0.4279950
47	6	0	-1.6434390	-0.9663850	-1.4275510
48	16	0	-2.3766110	-2.4866490	0.5425090
49	6	0	-3.0570500	-0.9022900	-1.3950550
50	1	0	-1.0293870	-0.3990300	-2.1239200
51	6	0	-3.6298920	-1.6540700	-0.3748350
52	1	0	-3.6501610	-0.2753630	-2.0577360
53	6	0	-5.0233200	-1.7736810	-0.0063390
54	6	0	-5.5779640	-2.2017420	1.1970760
55	16	0	-6.2986100	-1.3212330	-1.1327620
56	6	0	-7.0022810	-2.1523350	1.2153260
57	1	0	-4.9684960	-2.5133980	2.0440310
58	6	0	-7.5373420	-1.6891960	0.0296700
59	1	0	-7.6097370	-2.4386170	2.0726710
60	1	0	-8.5826100	-1.5473080	-0.2306840

Section S3. Conformational analysis

Each conformer of the monomeric or dimeric oligothiophenes was named according to the examples shown in figure S28.
In the following tables E_{rel}(intra) is the intramolecular relative energy between conformers as defined by figure 7 in the main article, i.e. the energy difference that arises solely from the relative configuration of all S atoms in each oligothiophene molecule; ΔE_{int}(dimer) is the self-association interaction energy calculated for each dimer as explained in the main article; and E_{rel}(total) = E_{rel}(intra) + ΔE_{int}(dimer), is the total relative energy of the given comformer.

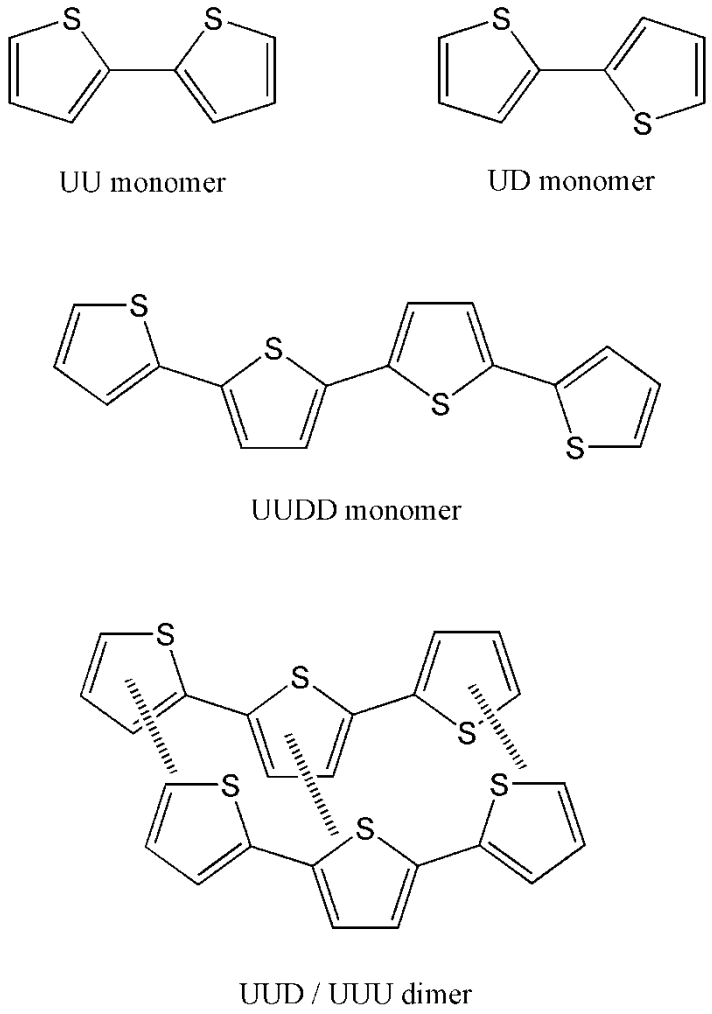

Figure S28. Some examples of conformer designation for the monomers and dimers of the oligothiophenes studied.

Table S52. Conformational analysis results for thiophene monomer.

Monomer	E_{rel}(intra) / kJ·mol^{-1}	p_i	$p_i \cdot \ln(p_i)$
U	0.0	1.00	0.00

Table S53. Conformational analysis results for thiophene dimer.

Dimer	E_{rel}(intra) / kJ·mol^{-1}	ΔE_{int}(dimer) / kJ·mol^{-1}	E_{rel}(total) / kJ·mol^{-1}	p_i	$p_i \cdot \ln(p_i)$
A	0	-8.1	-8.1	0.05	-0.15
B	0	-8.8	-8.8	0.07	-0.18
C	0	-9.2	-9.2	0.08	-0.20
D	0	-4.6	-4.6	0.01	-0.05
E	0	-9.7	-9.7	0.10	-0.22
F	0	-12.6	-12.6	0.31	-0.36
G	0	-11.5	-11.5	0.20	-0.32
H	0	-11.4	-11.4	0.19	-0.32

Table S54. Conformational analysis results for the thermodynamics of self-association of thiophene.

	monomer	dimer	Self-association reaction	
H_m / kJ·mol^{-1}	0.00	-11.02	$\Delta_{ass}H_m$ / kJ·mol^{-1}	-11.02
$S_{m,conf}$ / J·K^{-1}·mol^{-1}	0.00	15.03	$\Delta_{ass}S_{m,conf}$ / J·K^{-1}·mol^{-1}	15.03

Table S55. Conformational analysis results for 22-BT monomer.

Monomer	E_{rel}(intra) / kJ·mol^{-1}	p_i	$p_i \cdot \ln(p_i)$
UU	1.6	0.34	-0.37
UD	0.0	0.66	-0.28

Table S56. Conformational analysis results for 22-BT dimer.

Dimer		E_{rel}(intra) / kJ·mol^{-1}	ΔE_{int}(dimer) / kJ·mol^{-1}	E_{rel}(total) / kJ·mol^{-1}	p_i	$p_i \cdot \ln(p_i)$
UU /	UU	3.2	-26.0	-22.8	0.09	-0.21
	UD	1.6	-26.0	-24.4	0.17	-0.30
	DD	3.2	-26.0	-22.8	0.09	-0.21
UD /	UD	0.0	-26.0	-26.0	0.33	-0.37
	DU	0.0	-26.0	-26.0	0.33	-0.37

Table S57. Conformational analysis results for the thermodynamics of self-association of 22-BT.

	monomer	dimer	Self-association reaction	
H_m / kJ·mol^{-1}	0.55	-25.16	$\Delta_{ass}H_m$ / kJ·mol^{-1}	-26.26
$S_{m,conf}$ / J·K^{-1}·mol^{-1}	5.34	12.15	$\Delta_{ass}S_{m,conf}$ / J·K^{-1}·mol^{-1}	1.46

Table S58. Conformational analysis results for 2252-TT monomer.

Monomer	E_{rel}(intra) / kJ·mol^{-1}	p_i	p_i·ln(p_i)
UUU	3.2	0.15	-0.29
UUD	1.6	0.29	-0.36
UDU	0.0	0.56	-0.33

Table S59. Conformational analysis results for 2252-TT dimer.

Dimer		E_{rel}(intra) / kJ·mol^{-1}	ΔE_{int}(dimer) / kJ·mol^{-1}	E_{rel}(total) / kJ·mol^{-1}	p_i	p_i·ln(p_i)
UUU /	UUU	6.4	-40.0	-33.6	0.01	-0.06
	UUD	4.8	-40.0	-35.2	0.03	-0.10
	UDD	4.8	-40.0	-35.2	0.03	-0.10
	UDU	3.2	-40.0	-36.8	0.05	-0.16
	DUD	3.2	-40.0	-36.8	0.05	-0.16
	DDD	6.4	-40.0	-33.6	0.01	-0.06
	UUD	3.2	-40.0	-36.8	0.05	-0.16
	UDD	3.2	-40.0	-36.8	0.05	-0.16
UUD /	UDU	1.6	-40.0	-38.4	0.10	-0.23
	DDU	3.2	-40.0	-36.8	0.05	-0.16
	DUU	3.2	-40.0	-36.8	0.05	-0.16
	DUD	1.6	-40.0	-38.4	0.10	-0.23
UDU /	UDU	0.0	-40.0	-40.0	0.20	-0.32
	DUD	0.0	-40.0	-40.0	0.20	-0.32

Table S60. Conformational analysis results for the thermodynamics of self-association of 2252-TT.

	monomer	dimer	Self-association reaction	
H_m / kJ·mol^{-1}	0.95	-38.20	$\Delta_{ass}H_m$ / kJ·mol^{-1}	-40.10
$S_{m,conf}$ / J·K^{-1}·mol^{-1}	8.07	19.64	$\Delta_{ass}S_{m,conf}$ / J·K^{-1}·mol^{-1}	3.51

Table S61. Conformational analysis results for α-quaterthiophene monomer.

Monomer	E_{rel}(intra) / kJ·mol^{-1}	p_i	p_i·ln(p_i)
UUUU	4.8	0.05	-0.15
UUUD	3.2	0.10	-0.23
UUDD	3.2	0.10	-0.23
UUDU	1.6	0.19	-0.32
UDDU	1.6	0.19	-0.32
UDUD	0.0	0.37	-0.37

Table S62. Conformational analysis results for α-quaterthiophene dimer.

Dimer		E_{rel}(intra) / kJ·mol^{-1}	ΔE_{int}(dimer) / kJ·mol^{-1}	E_{rel}(total) / kJ·mol^{-1}	p_i	$p_i \cdot \ln(p_i)$
UUUU /	UUUU	9.6	-55.0	-45.4	0.00	-0.02
	UUUD	8.0	-55.0	-47.0	0.01	-0.03
	UUDD	8.0	-40.0	-32.0	0.00	0.00
	UDDD	8.0	-40.0	-32.0	0.00	0.00
	DDDD	9.6	-40.0	-30.4	0.00	0.00
	DUUD	6.4	-55.0	-48.6	0.01	-0.05
	DUDD	6.4	-40.0	-33.6	0.00	0.00
	DUDU	4.8	-40.0	-35.2	0.00	0.00
	UDDU	6.4	-40.0	-33.6	0.00	0.00
	UDUU	6.4	-55.0	-48.6	0.01	-0.05
UUUD /	UUUD	6.4	-55.0	-48.6	0.01	-0.05
	UUDD	6.4	-40.0	-33.6	0.00	0.00
	UDDD	6.4	-40.0	-33.6	0.00	0.00
	DDDU	6.4	-40.0	-33.6	0.00	0.00
	DDUU	6.4	-55.0	-48.6	0.01	-0.05
	DUUU	6.4	-55.0	-48.6	0.01	-0.05
	DUUD	4.8	-55.0	-50.2	0.02	-0.09
	DUDD	4.8	-40.0	-35.2	0.00	0.00
	DUDU	3.2	-40.0	-36.8	0.00	0.00
	UDDU	4.8	-40.0	-35.2	0.00	0.00
	UDUU	4.8	-40.0	-35.2	0.00	0.00
	UDUD	3.2	-40.0	-36.8	0.00	0.00
	DDUD	4.8	-40.0	-35.2	0.00	0.00
	UUDU	4.8	-40.0	-35.2	0.00	0.00
UUDD /	UUDD	6.4	-55.0	-48.6	0.01	-0.05
	DDUU	6.4	-55.0	-48.6	0.01	-0.05
	DUUD	4.8	-40.0	-35.2	0.00	0.00
	DUDD	4.8	-55.0	-50.2	0.02	-0.09
	DUDU	3.2	-55.0	-51.8	0.05	-0.14
	UDUU	4.8	-55.0	-50.2	0.02	-0.09
	UDUD	3.2	-55.0	-51.8	0.05	-0.14
UUDU /	DUUD	3.2	-40.0	-36.8	0.00	0.00
	DUDD	3.2	-55.0	-51.8	0.05	-0.14
	DUDU	1.6	-55.0	-53.4	0.09	-0.21
	UDDU	3.2	-40.0	-36.8	0.00	0.00
	UDUU	3.2	-55.0	-51.8	0.05	-0.14
	UDUD	1.6	-55.0	-53.4	0.09	-0.21
	DDUD	3.2	-55.0	-51.8	0.05	-0.14
	UUDU	3.2	-55.0	-51.8	0.05	-0.14
UDDU /	DUUD	3.2	-40.0	-36.8	0.00	0.00
	DUDU	1.6	-40.0	-38.4	0.00	0.00
	UDDU	3.2	-55.0	-51.8	0.05	-0.14
UDUD /	DUDU	0.0	-55.0	-55.0	0.17	-0.30
	UDUD	0.0	-55.0	-55.0	0.17	-0.30

Table S63. Conformational analysis results for the thermodynamics of self-association of α-quaterthiophene.

	monomer	dimer	Self-association reaction	
H_m / kJ·mol^{-1}	1.50	-52.69	$\Delta_{ass}H_m$ / kJ·mol^{-1}	-55.69
$S_{m,conf}$ / J·K^{-1}·mol^{-1}	13.41	22.64	$\Delta_{ass}S_{m,conf}$ / J·K^{-1}·mol^{-1}	-4.18