Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information (SI)

Cooperativity Between Hydrogen- and Halogen Bonds: the Case of Selenourea

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Titration studies.

Benzoate + **I1**

Table S1. ^{19}F chemical shift of the αF of **I1** (22.6 mM) at different concentrations of [**TBABzO**].

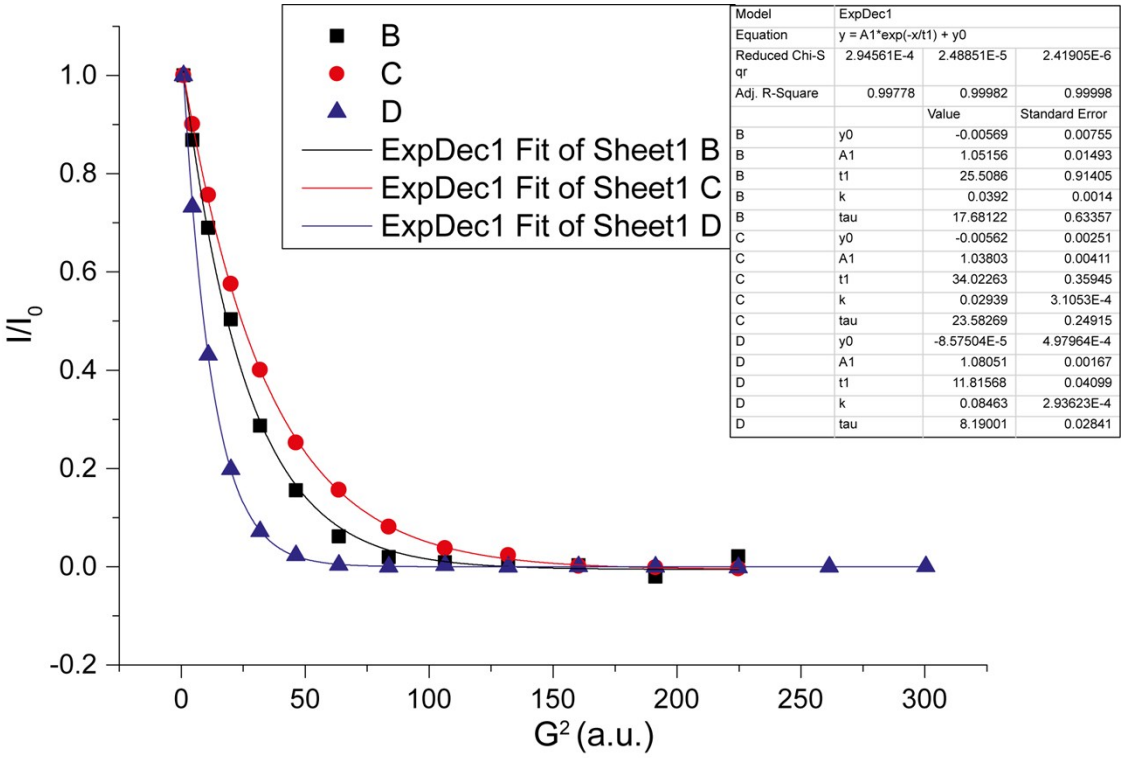
[**TBABzO**] (M)	$\delta_{\alpha F}$(**I1**) (ppm)
0	-65,1614
0,0134	-70,5373
0,0176	-71,8447
0,0192	-72,159
0,0247	-73,4476
0,03	-74,361
0,036	-75,1553
0,047	-76,0039
0,0747	-77,0226
0,00062	-65,3094
0,0021	-66,206
0,0046	-67,0994
0,0092	-69,0357

Table S2. ^{1}H chemical shift of the NH (a and b) of **SeU** (64 mM) at different concentrations of [**TBABzO**].

[**TBABzO**] (M)	δ_{NHa}(**SeU**) (ppm)	δ_{NHb}(**SeU**) (ppm)	averaged $\delta_{NHa,b}$(**SeU**) (ppm)
0	[a]	[a]	7,2633
0,0011	[a]	[a]	7,301
0,00185	[a]	[a]	7,31
0,00232	7,382	7,27	7,326
0,00366	7,498	7,198	7,348
0,00529	7,6154	7,1621	7,38875
0,00706	7,7309	7,1264	7,42865
0,00919	7,8361	7,1165	7,4763
0,01123	7,973	7,0851	7,52905
0,01194	8,003	7,0728	7,5379
0,01393	8,1369	7,0454	7,59115
0,01736	8,3132	7,0239	7,66855
0,0198	8,4553	6,992	7,72365
0,02198	8,5753	6,971	7,77315
0,02343	8,6519	6,9546	7,80325
0,02815	8,9529	6,8914	7,92215
0,03337	9,2298	6,8538	8,0418
0,04514	9,9484	6,727	8,3377
0,04954	10,2051	6,6848	8,44495
0,06337	10,9646	6,5673	8,76595
0,08337	11,3006	6,529	8,9148
0,1078	11,3122	6,5491	8,93065

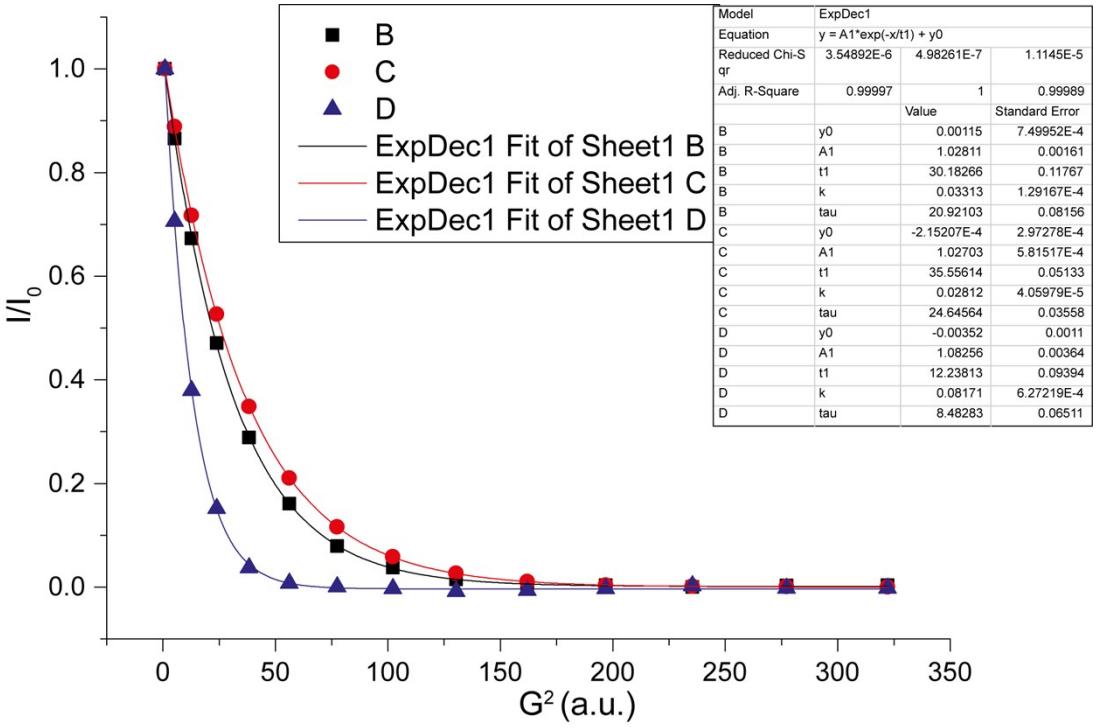
[a]The two peaks overlap, showing the same δ (the averaged one).

Diffusion NMR studies.



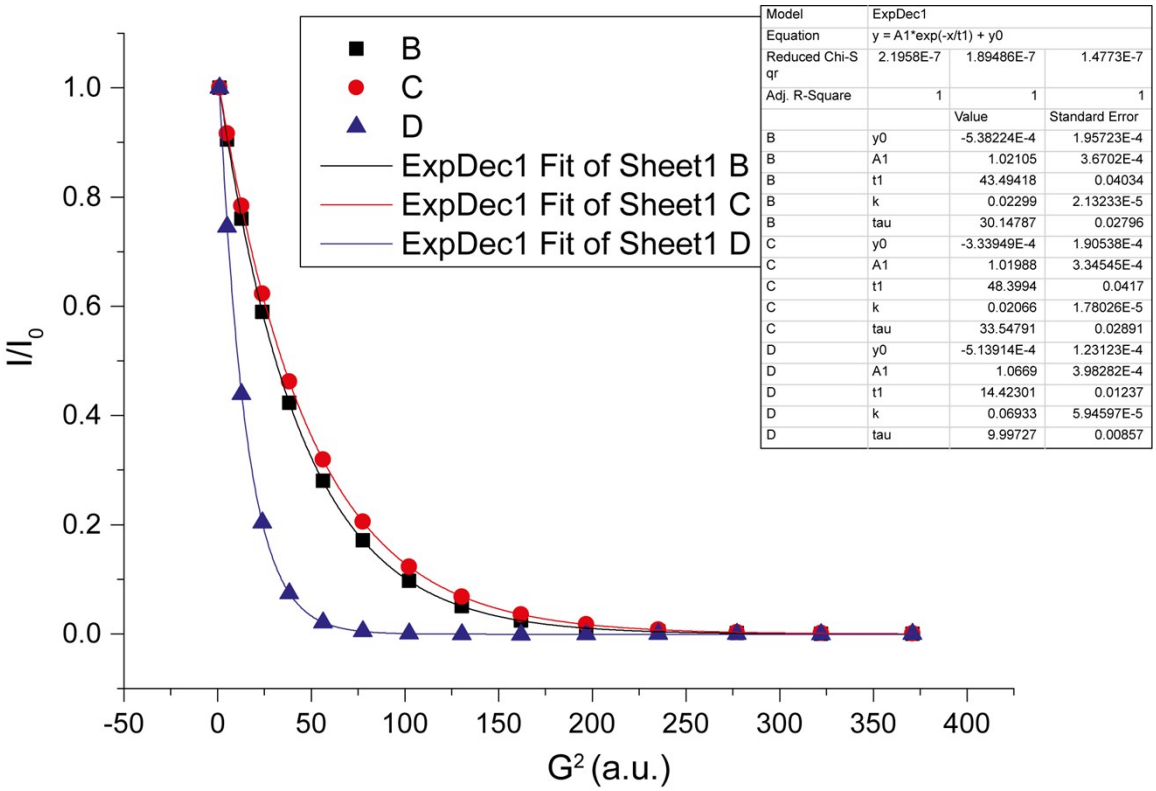
Model	ExpDec1		
Equation	y = A1*exp(-x/t1) + y0		
Reduced Chi-Sqr	2.94561E-4	2.48851E-5	2.41905E-6
Adj. R-Square	0.99778	0.99982	0.99998
		Value	Standard Error
B	y0	-0.00569	0.00755
B	A1	1.05156	0.01493
B	t1	25.5086	0.91405
B	k	0.0392	0.0014
B	tau	17.68122	0.63357
C	y0	-0.00562	0.00251
C	A1	1.03803	0.00411
C	t1	34.02263	0.35945
C	k	0.02939	3.1053E-4
C	tau	23.58269	0.24915
D	y0	-8.57504E-5	4.97964E-4
D	A1	1.08051	0.00167
D	t1	11.81568	0.04099
D	k	0.08463	2.93623E-4
D	tau	8.19001	0.02841

Figure S1. I/I_0 versus G^2 for **TBABzO** in acetone-d6 (C = 2.5 mM). B = benzoate; C = Tetrabutylammonium; D = solvent.



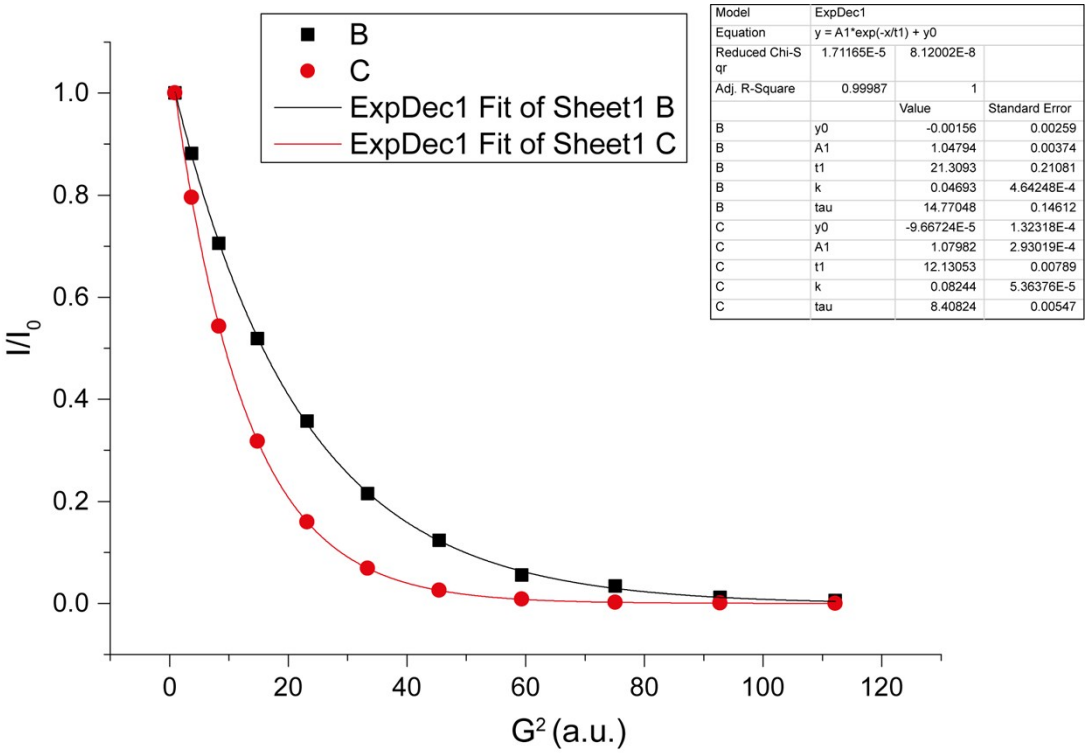
Model	ExpDec1		
Equation	y = A1*exp(-x/t1) + y0		
Reduced Chi-Sqr	3.54892E-6	4.98261E-7	1.1145E-5
Adj. R-Square	0.99997	1	0.99989
		Value	Standard Error
B	y0	0.00115	7.49952E-4
B	A1	1.02811	0.00161
B	t1	30.18266	0.11767
B	k	0.03313	1.29167E-4
B	tau	20.92103	0.08156
C	y0	-2.15207E-4	2.97278E-4
C	A1	1.02703	5.81517E-4
C	t1	35.55614	0.05133
C	k	0.02812	4.05979E-5
C	tau	24.64564	0.03558
D	y0	-0.00352	0.0011
D	A1	1.08256	0.00364
D	t1	12.23813	0.09394
D	k	0.08171	6.27219E-4
D	tau	8.48283	0.06511

Figure S2 I/I_0 versus G^2 for **TBABzO** in acetone-d6 (C = 20.5 mM). B = benzoate; C = Tetrabutylammonium; D = solvent.



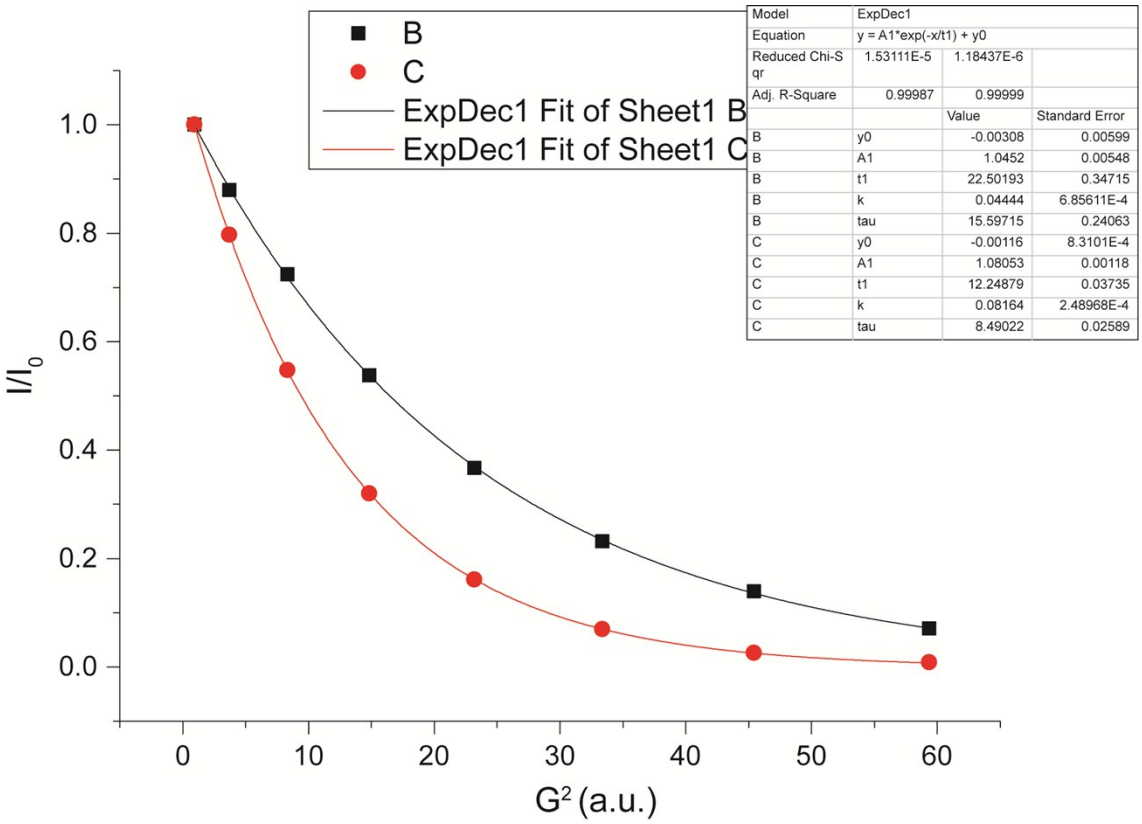
Model	ExpDec1		
Equation	y = A1*exp(-x/t1) + y0		
Reduced Chi-Sqr	2.1958E-7	1.89486E-7	1.4773E-7
Adj. R-Square	1	1	1
		Value	Standard Error
B	y0	-5.38224E-4	1.95723E-4
B	A1	1.02105	3.6702E-4
B	t1	43.49418	0.04034
B	k	0.02299	2.13233E-5
B	tau	30.14787	0.02796
C	y0	-3.33949E-4	1.90538E-4
C	A1	1.01988	3.34545E-4
C	t1	48.3994	0.0417
C	k	0.02066	1.78026E-5
C	tau	33.54791	0.02891
D	y0	-5.13914E-4	1.23123E-4
D	A1	1.0669	3.98282E-4
D	t1	14.42301	0.01237
D	k	0.06933	5.94597E-5
D	tau	9.99727	0.00857

Figure S3 I/I_0 versus G^2 for **TBABzO** in acetone-d6 (C = 185 mM). B = benzoate; C = Tetrabutylammonium; D = solvent.



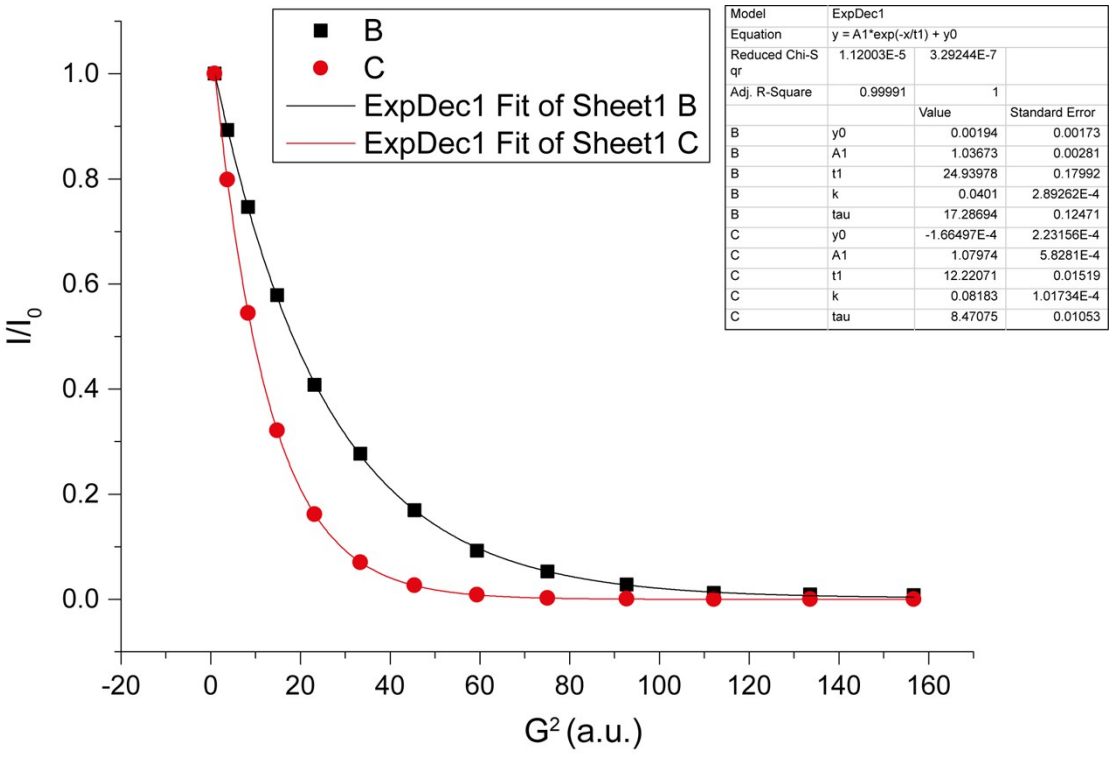
Model	ExpDec1		
Equation	y = A1*exp(-x/t1) + y0		
Reduced Chi-Sqr	1.71165E-5	8.12002E-8	
Adj. R-Square	0.99987	1	
		Value	Standard Error
B	y0	-0.00156	0.00259
B	A1	1.04794	0.00374
B	t1	21.3093	0.21081
B	k	0.04693	4.64248E-4
B	tau	14.77048	0.14612
C	y0	-9.66724E-5	1.32318E-4
C	A1	1.07982	2.93019E-4
C	t1	12.13053	0.00789
C	k	0.08244	5.36376E-5
C	tau	8.40824	0.00547

Figure S4 I/I_0 versus G^2 for **SeU** in acetone-d6 (C = 16 mM). B = **SeU**; C = solvent.



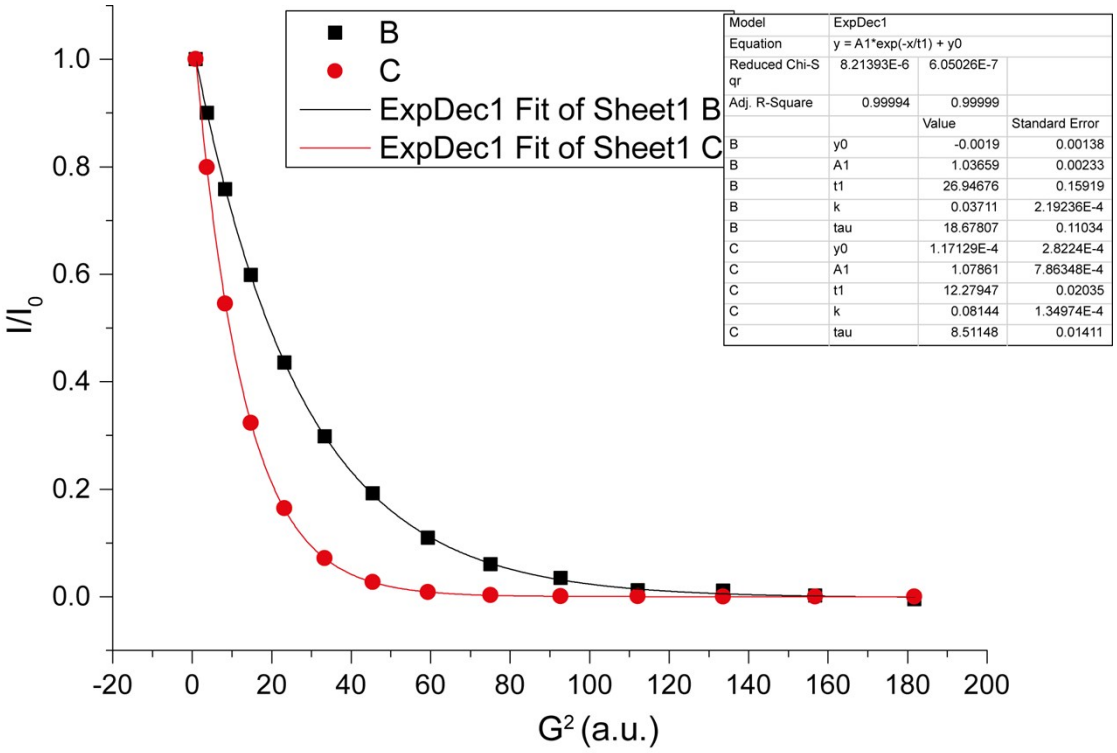
Model	ExpDec1		
Equation	y = A1*exp(-x/t1) + y0		
Reduced Chi-Sqr	1.53111E-5	1.18437E-6	
Adj. R-Square	0.99987	0.99999	
		Value	Standard Error
B	y0	-0.00308	0.00599
B	A1	1.0452	0.00548
B	t1	22.50193	0.34715
B	k	0.04444	6.85611E-4
B	tau	15.59715	0.24063
C	y0	-0.00116	8.3101E-4
C	A1	1.08053	0.00118
C	t1	12.24879	0.03735
C	k	0.08164	2.48968E-4
C	tau	8.49022	0.02589

Figure S5 I/I_0 versus G^2 for **SeU** in acetone-d6 (C = 16 mM) + **I1** (19 mM). B = **SeU**; C = solvent.



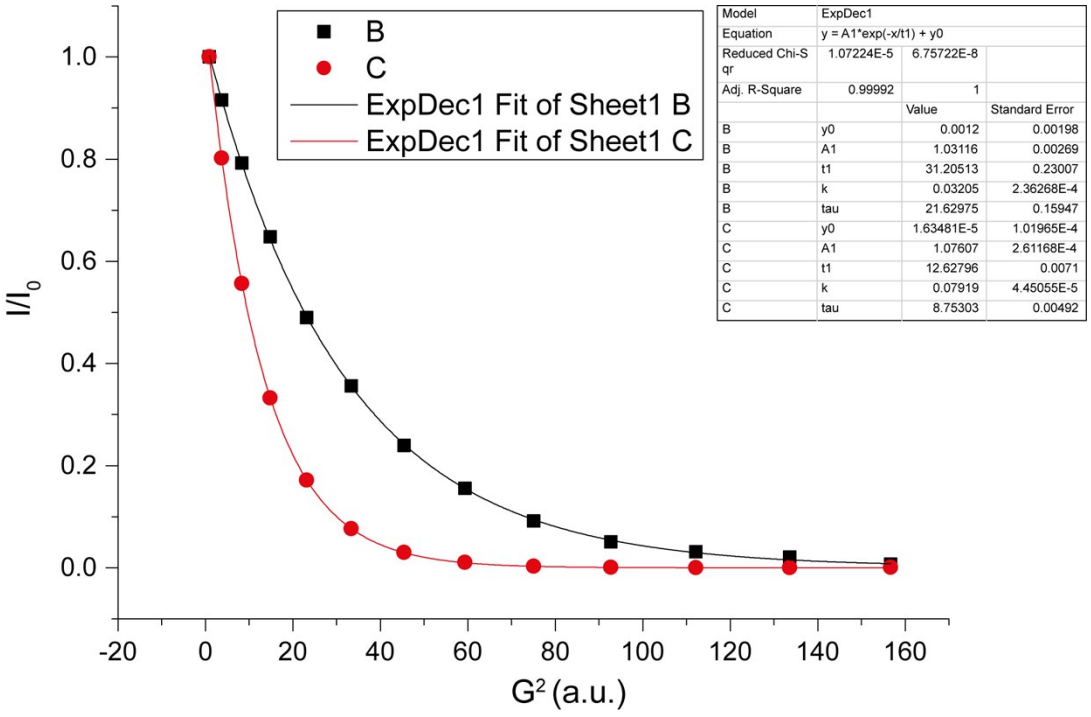
Model	ExpDec1		
Equation	y = A1*exp(-x/t1) + y0		
Reduced Chi-Sqr	1.12003E-5	3.29244E-7	
Adj. R-Square	0.99991	1	
		Value	Standard Error
B	y0	0.00194	0.00173
B	A1	1.03673	0.00281
B	t1	24.93978	0.17992
B	k	0.0401	2.89262E-4
B	tau	17.28694	0.12471
C	y0	-1.66497E-4	2.23156E-4
C	A1	1.07974	5.8281E-4
C	t1	12.22071	0.01519
C	k	0.08183	1.01734E-4
C	tau	8.47075	0.01053

Figure S6 I/I_0 versus G^2 for **SeU** in acetone-d6 (C = 16 mM) + **I1** (82 mM). B = **SeU**; C = solvent.



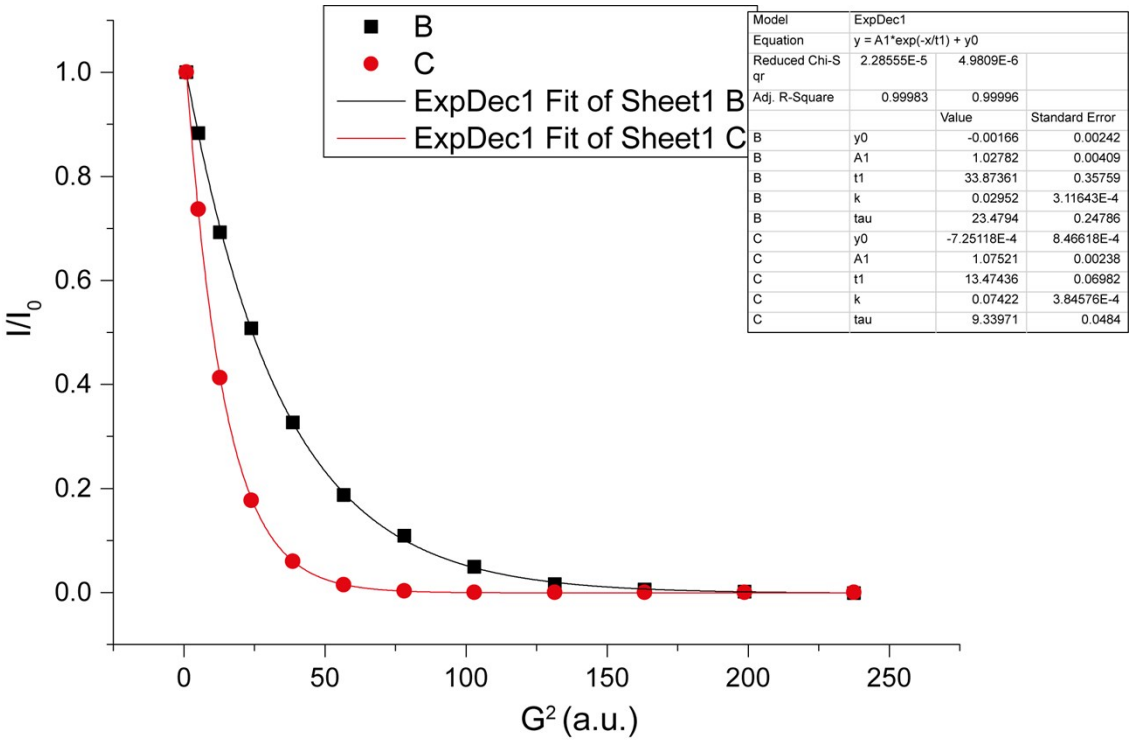
Model	ExpDec1		
Equation	y = A1*exp(-x/t1) + y0		
Reduced Chi-Sqr	8.21393E-6	6.05026E-7	
Adj. R-Square	0.99994	0.99999	
		Value	Standard Error
B	y0	-0.0019	0.00138
B	A1	1.03659	0.00233
B	t1	26.94676	0.15919
B	k	0.03711	2.19236E-4
B	tau	18.67807	0.11034
C	y0	1.17129E-4	2.8224E-4
C	A1	1.07861	7.86348E-4
C	t1	12.27947	0.02035
C	k	0.08144	1.34974E-4
C	tau	8.51148	0.01411

Figure S7 I/I_0 versus G^2 for **SeU** in acetone-d6 (C = 16 mM) + **I1** (209 mM). B = **SeU**; C = solvent.



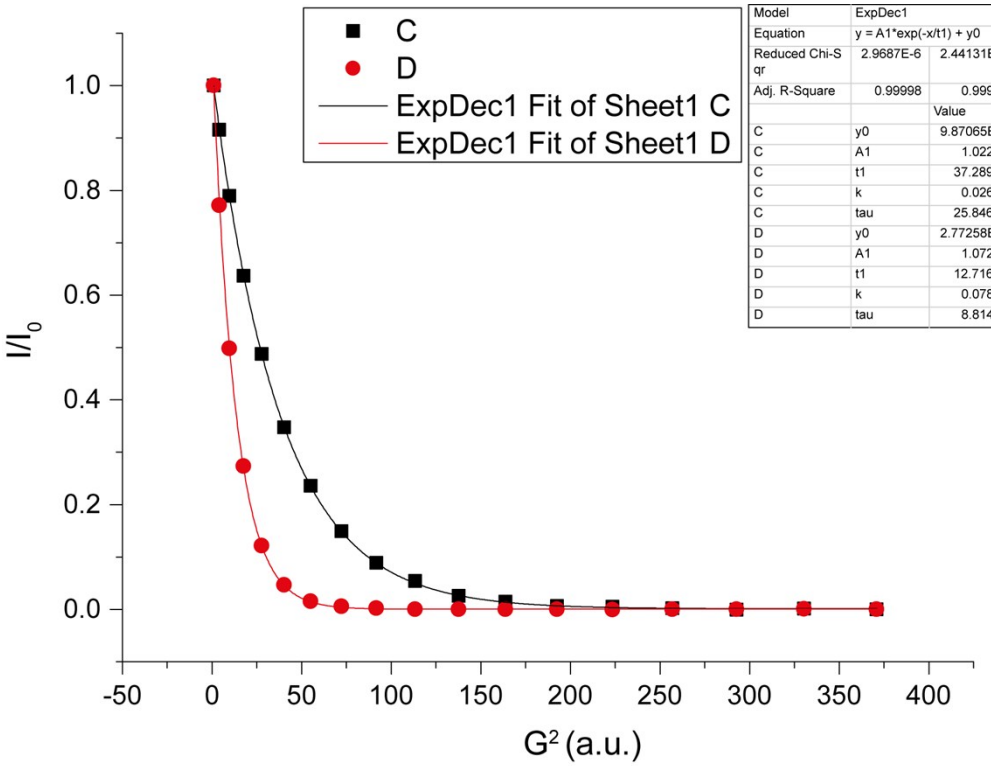
Model	ExpDec1		
Equation	y = A1*exp(-x/t1) + y0		
Reduced Chi-Sqr	1.07224E-5	6.75722E-8	
Adj. R-Square	0.99992	1	
		Value	Standard Error
B	y0	0.0012	0.00198
B	A1	1.03116	0.00269
B	t1	31.20513	0.23007
B	k	0.03205	2.36268E-4
B	tau	21.62975	0.15947
C	y0	1.63481E-5	1.01965E-4
C	A1	1.07607	2.61168E-4
C	t1	12.62796	0.0071
C	k	0.07919	4.45055E-5
C	tau	8.75303	0.00492

Figure S8 I/I_0 versus G^2 for **SeU** in acetone-d6 (C = 16 mM) + **I1** (460 mM). B = **SeU**; C = solvent.



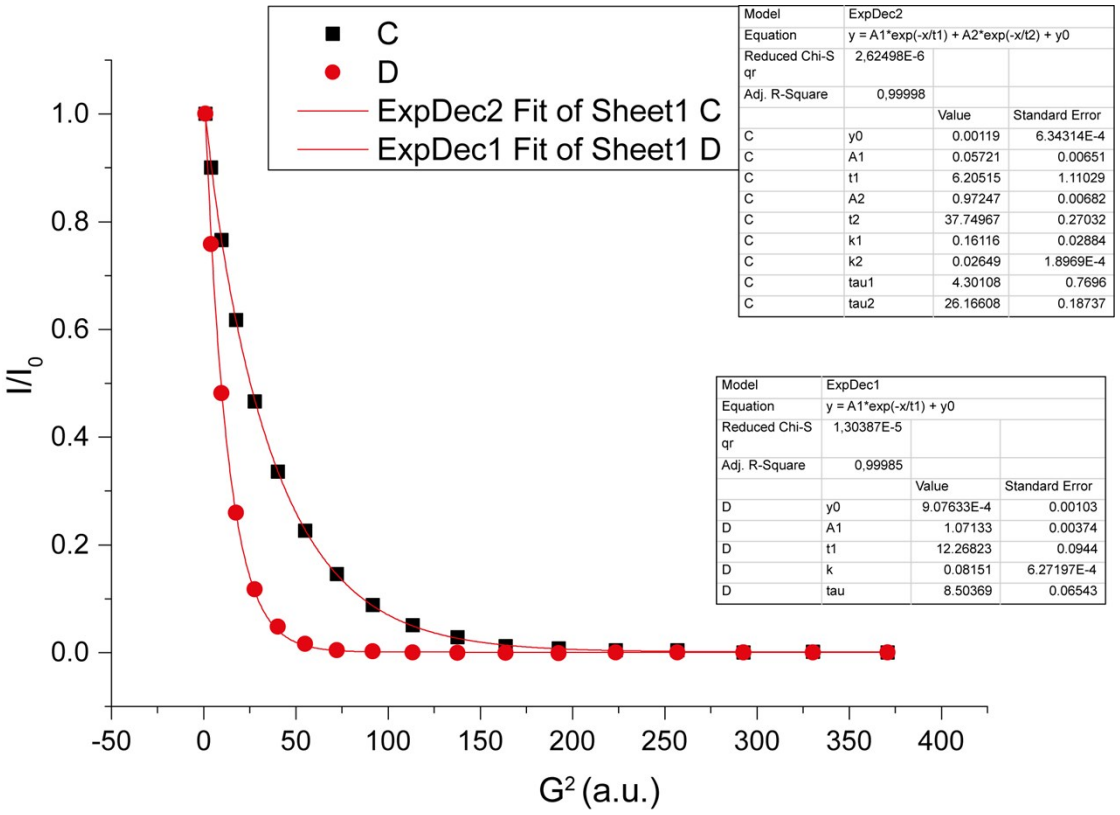
Model	ExpDec1		
Equation	y = A1*exp(-x/t1) + y0		
Reduced Chi-Sqr	2.28555E-5	4.9809E-6	
Adj. R-Square	0.99983	0.99996	
		Value	Standard Error
B	y0	-0.00166	0.00242
B	A1	1.02782	0.00409
B	t1	33.87361	0.35759
B	k	0.02952	3.11643E-4
B	tau	23.4794	0.24786
C	y0	-7.25118E-4	8.46618E-4
C	A1	1.07521	0.00238
C	t1	13.47436	0.06982
C	k	0.07422	3.84576E-4
C	tau	9.33971	0.0484

Figure S9 I/I_0 versus G^2 for **SeU** in acetone-d6 (C = 16 mM) + **I1** (931 mM). B = **SeU**; C = solvent.



Model	ExpDec1		
Equation	y = A1*exp(-x/t1) + y0		
Reduced Chi-Sqr	2.9687E-6	2.44131E-6	
Adj. R-Square	0.99998	0.99997	
		Value	Standard Error
C	y0	9.87065E-4	6.21364E-4
C	A1	1.02272	0.00129
C	t1	37.28921	0.11754
C	k	0.02682	8.45313E-5
C	tau	25.84691	0.08147
D	y0	2.77258E-4	4.48882E-4
D	A1	1.07279	0.0016
D	t1	12.71639	0.04192
D	k	0.07864	2.59214E-4
D	tau	8.81433	0.02905

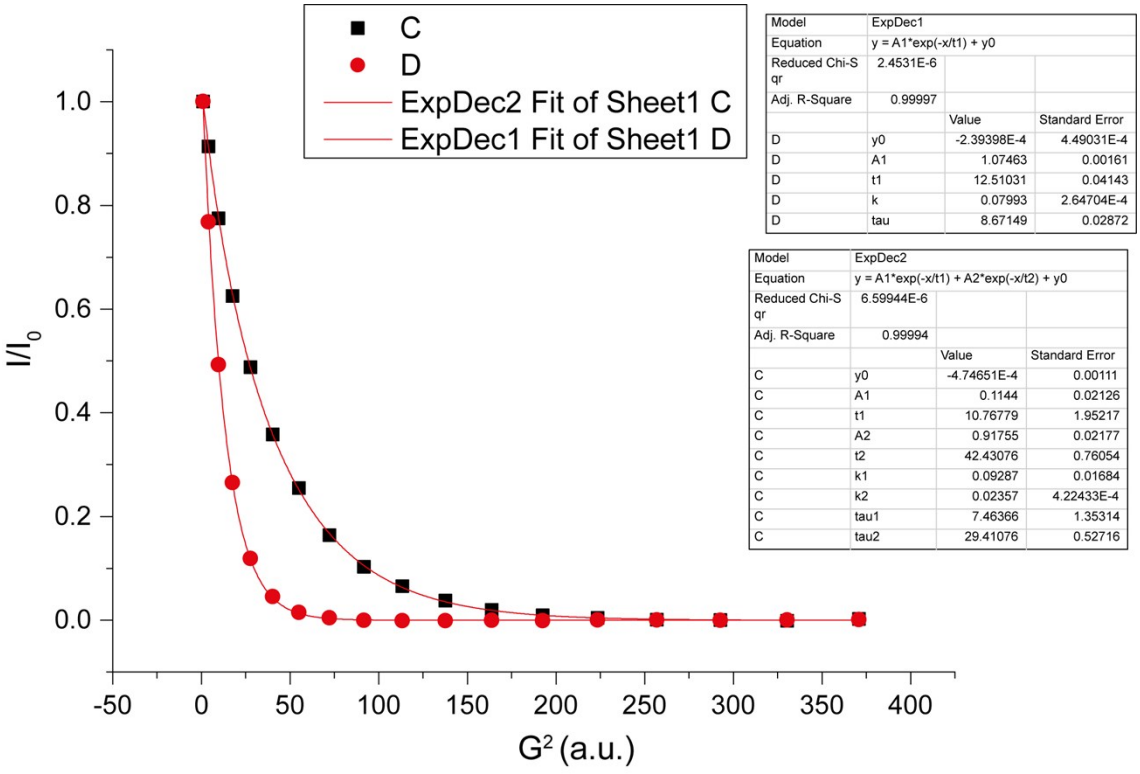
Figure S10. I/I_0 versus G^2 for **SeU** in acetone-d6 (C = 32 mM) + **TBABzO** (74 mM). B = **SeU**; C = solvent.



Model	ExpDec2		
Equation	y = A1*exp(-x/t1) + A2*exp(-x/t2) + y0		
Reduced Chi-Sqr	2,62498E-6		
Adj. R-Square	0,99998		
		Value	Standard Error
C	y0	0.00119	6.34314E-4
C	A1	0.05721	0.00651
C	t1	6.20515	1.11029
C	A2	0.97247	0.00682
C	t2	37.74967	0.27032
C	k1	0.16116	0.02884
C	k2	0.02649	1.8969E-4
C	tau1	4.30108	0.7696
C	tau2	26.16608	0.18737

Model	ExpDec1		
Equation	y = A1*exp(-x/t1) + y0		
Reduced Chi-Sqr	1,30387E-5		
Adj. R-Square	0,99985		
		Value	Standard Error
D	y0	9.07633E-4	0.00103
D	A1	1.07133	0.00374
D	t1	12.26823	0.0944
D	k	0.08151	6.27197E-4
D	tau	8.50369	0.06543

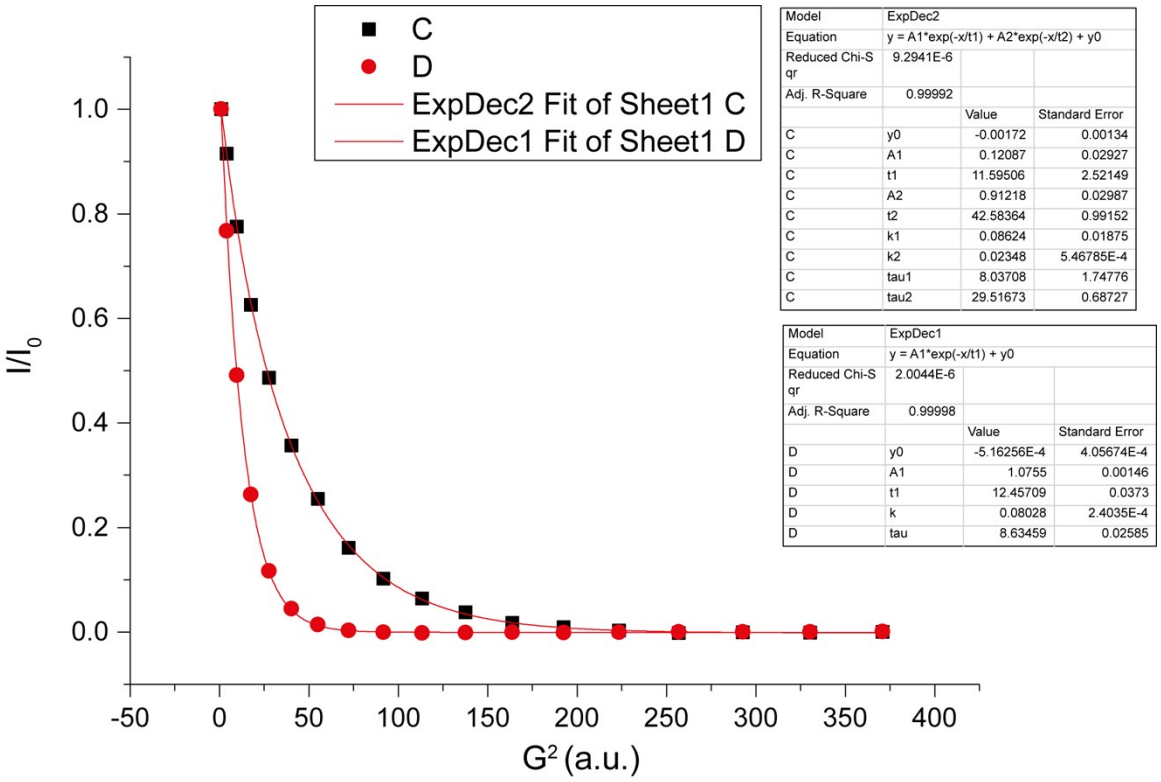
Figure S11. I/I_0 versus G^2 for **SeU** in acetone-d6 (C = 32 mM) + **TBABzO** (74 mM) + **I1** (16 mM). B = **SeU**; C = solvent.



Model	ExpDec1		
Equation	y = A1*exp(-x/t1) + y0		
Reduced Chi-Sqr	2.4531E-6		
Adj. R-Square	0.99997		
		Value	Standard Error
D	y0	-2.39398E-4	4.49031E-4
D	A1	1.07463	0.00161
D	t1	12.51031	0.04143
D	k	0.07993	2.64704E-4
D	tau	8.67149	0.02872

Model	ExpDec2		
Equation	y = A1*exp(-x/t1) + A2*exp(-x/t2) + y0		
Reduced Chi-Sqr	6.59944E-6		
Adj. R-Square	0.99994		
		Value	Standard Error
C	y0	-4.74651E-4	0.00111
C	A1	0.1144	0.02126
C	t1	10.76779	1.95217
C	A2	0.91755	0.02177
C	t2	42.43076	0.76054
C	k1	0.09287	0.01684
C	k2	0.02357	4.22433E-4
C	tau1	7.46366	1.35314
C	tau2	29.41076	0.52716

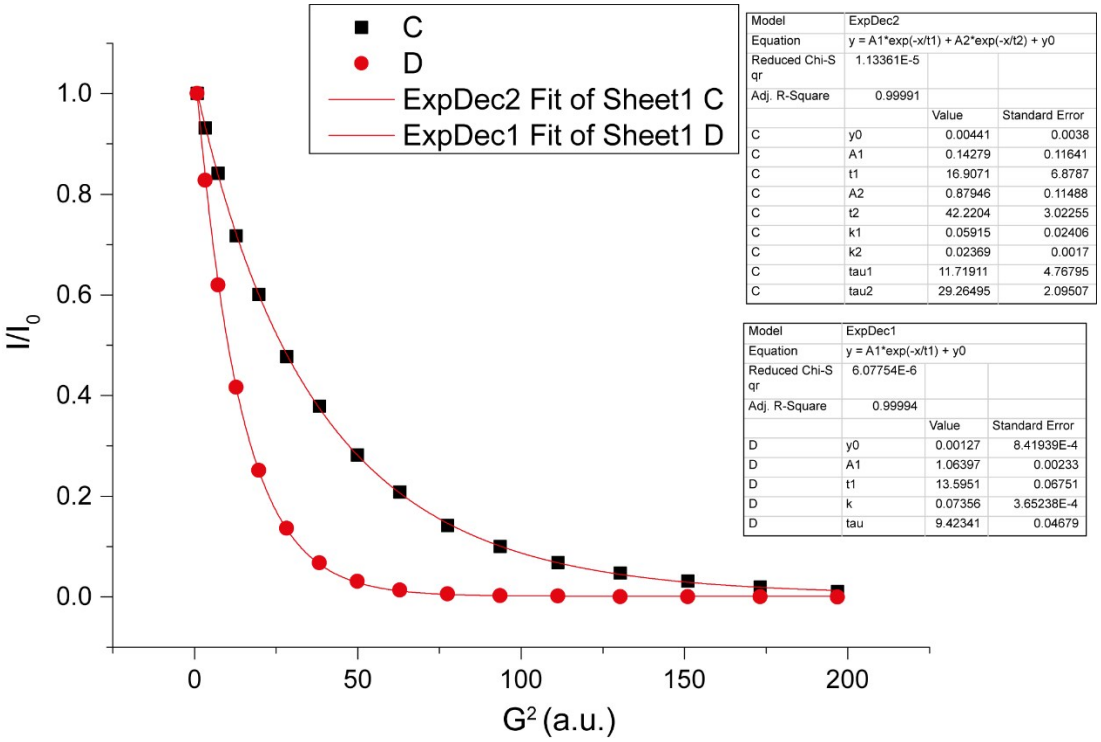
Figure S12. I/I_0 versus G^2 for **SeU** in acetone-d6 (C = 32 mM) + **TBABzO** (74 mM) + **I1** (30 mM). B = **SeU**; C = solvent.



Model	ExpDec2		
Equation	y = A1*exp(-x/t1) + A2*exp(-x/t2) + y0		
Reduced Chi-Sqr	9.2941E-6		
Adj. R-Square	0.99992		
		Value	Standard Error
C	y0	-0.00172	0.00134
C	A1	0.12087	0.02927
C	t1	11.59506	2.52149
C	A2	0.91218	0.02987
C	t2	42.58364	0.99152
C	k1	0.08624	0.01875
C	k2	0.02348	5.46785E-4
C	tau1	8.03708	1.74776
C	tau2	29.51673	0.68727

Model	ExpDec1		
Equation	y = A1*exp(-x/t1) + y0		
Reduced Chi-Sqr	2.0044E-6		
Adj. R-Square	0.99998		
		Value	Standard Error
D	y0	-5.16256E-4	4.05674E-4
D	A1	1.0755	0.00146
D	t1	12.45709	0.0373
D	k	0.08028	2.4035E-4
D	tau	8.63459	0.02585

Figure S13 I/I_0 versus G^2 for **SeU** in acetone-d6 (C = 32 mM) + **TBABzO** (74 mM) + **I1** (52.8 mM). B = **SeU**; C = solvent.



Model	ExpDec2		
Equation	y = A1*exp(-x/t1) + A2*exp(-x/t2) + y0		
Reduced Chi-Sqr	1.13361E-5		
Adj. R-Square	0.99991		
		Value	Standard Error
C	y0	0.00441	0.0038
C	A1	0.14279	0.11641
C	t1	16.9071	6.8787
C	A2	0.87946	0.11488
C	t2	42.2204	3.02255
C	k1	0.05915	0.02406
C	k2	0.02369	0.0017
C	tau1	11.71911	4.76795
C	tau2	29.26495	2.09507

Model	ExpDec1		
Equation	y = A1*exp(-x/t1) + y0		
Reduced Chi-Sqr	6.07754E-6		
Adj. R-Square	0.99994		
		Value	Standard Error
D	y0	0.00127	8.41939E-4
D	A1	1.06397	0.00233
D	t1	13.5951	0.06751
D	k	0.07356	3.65238E-4
D	tau	9.42341	0.04679

Figure S14 I/I_0 versus G^2 for **SeU** in acetone-d6 (C = 32 mM) + **TBABzO** (74 mM) + **I1** (248 mM). B = **SeU**; C = solvent.

Table S3. Interaction energy (in kcal/mol), thermodynamic parameters and bond lengths (in Å) for the different adducts at M06-2X/aug-TZVP//BP86-D3/aug-TZVP level (gas phase). The parenthesis indicate that the interaction energy is referred to the pre-formed binary adduct rather than the three isolated components.

Adduct	ΔE	ΔH^a	ΔS^a	ΔG^a	C-Se	C-N
SeU	-	-	-	-	1.830	1.366
S-I$_m$	-6.2	-5.9	-10.3	4.4	1.855	1.351[b]
B-S	-39.4	-41.3	-14.1	-25.5	1.881	1.344
B-I$_m$	-21.6	-21.4	-13.2	-8.1	-	-
B-S-I$_m$	-52.4	-54.3	-29.3	-25.0	1.903	1.334[b]
(B-S)-I$_m$	-13.0	-12.9	-13.5	0.6	-	-
B-(S-I$_m$)	-46.2	-48.4	-19.0	-29.3	-	-

[a] Calculated at 298 K; [b] Averaged between the two CN bonds

Table S4. Relevant donor – acceptor (D → A) natural bond orbital interactions and their second-order perturbation stabilization energies ($E^{(2)}$, in kcal/mol) for halogen- and hydrogen bonds in **S-I$_m$**, **B-S** and **B-S-I$_m$** adducts.

Adduct	D → A interaction	$E^{(2)}$
S-I$_m$	LP(1)Se2 → BD*(1)I9C10	1.37
	LP(2)Se2 → BD*(1)I9C10	25.04
	LP(1)N3 → BD*(1)C1Se2	82.66
	LP(1)N6 → BD*(1)C1Se2	72.89
	LP(3)I9 → BD*(1)N3H4	4.51
	BD(1)C1Se2 → RY(2)I9	0.23
B-S	LP(2)O21 → BD*(1)N6H8	13.49
	LP(2)O22 → BD*(1)N3H4	13.46
	LP(2)Se2 → LV(1)C1	349.15
	LP(1)N3 → LV(1)C1	161.99
	LP(1)N6 → LV(1)C1	163.03
B-S-I$_m$	LP(1)Se2 → BD*(1)I23C24	2.16
	LP(2)Se2 → BD*(1)I23C24	50.87
	LP(2)O21 → BD*(1)N6H8	17.81
	LP(2)O22 → BD*(1)N3H4	20.84
	LP(3)I23 → BD*(1)N6H7	1.80

LP(2)Se2 → LV(1)C1	178.79
LP(1)N6 → LV(1)C1	185.41
LP(1)N3 → LV(1)C1	177.85