Supporting Information for

Anion Photoelectron Spectroscopy of Rubrene: Molecular Insights into Singlet Fission Energetics

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Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; B. Mennucci; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09, Revision E.01*, Gaussian, Inc.: Wallingford CT, **2013**.

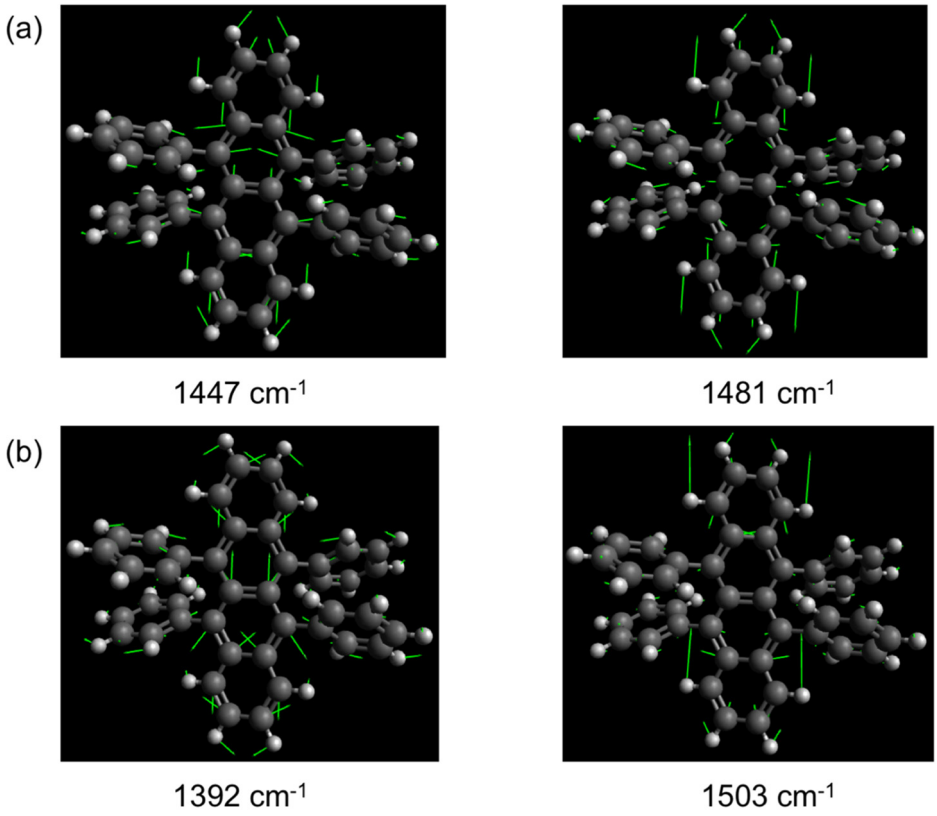

Figure S1. (a) Calculated vibrational modes with frequencies of ν_{150} (179 meV (1447 cm^{-1})) and ν_{152} (184 meV (1481 cm^{-1})) for the neutral RUB molecule for D_2 symmetry in the S_0 ground state. (b) Calculated vibrational modes with frequencies of ν_{150} (173 meV (1392 cm^{-1})) and ν_{159} (186 meV (1503 cm^{-1})) for the T_1 excited state. The vibrational modes are excited upon photodetachement since these vibrational modes are along the structural displacement between the anion and the neutral.

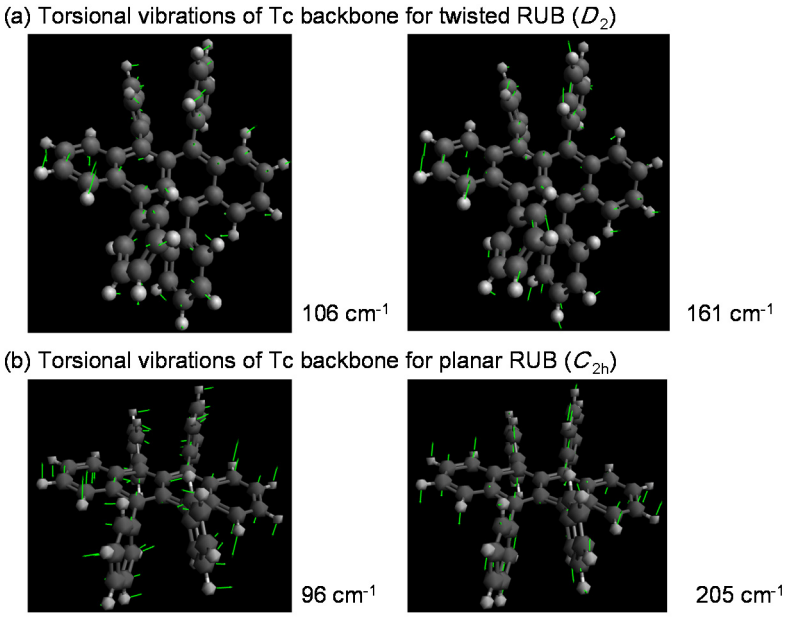

Figure S2. Calculated torsional vibrations with frequencies of 100-200 cm^{-1} for the neutral RUB molecule of (a) twisted Tc backbone (D_2) and (b) planar Tc backbone (C_{2h}) isomers calculated with B3LYP/6-311G(d).

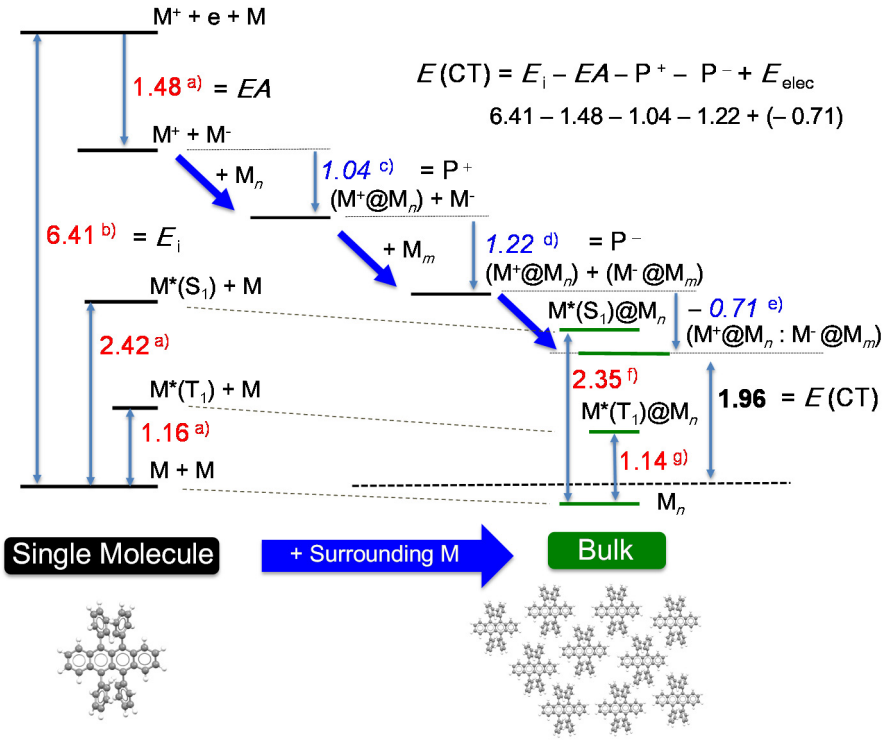

Figure S3. Scheme evaluating the charge-transfer (CT) energy, E(CT), in bulk. a) This work. b) Ionization energy, E_i, of the rubrene molecule (ref. 1). c) Polarization energy of the positive polaron, P^+; difference between E_i and the work function of the RUB film (refs. 2, 3) (= 6.41 – 5.37). d) Polarization energy of the negative polaron, P^-; difference between the IPES for LUMO (ref. 2) and EA (=2.7 – 1.48). e) Calculated Coulombic interaction of molecular ion pairs between $(RUB)^+@(RUB)_n$ and $(RUB)^-@(RUB)_n$, which stand for positive and negative polarons consisting of an ion core and surrounding molecules, respectively. (ref. 4). f) Fluorescence (refs. 5-7). g) Phosphorescence (refs. 8-10).

TABLE S1. Total energies and Cartesian coordinates (in Å).

Rubrene neutral (E = – 1617.65388018 Hartree): twisted (D_2)

C	-0.66281	-4.88612	-0.25990
C	0.66282	-4.88612	0.25985
C	1.31678	-3.70953	0.47647
C	0.69792	-2.44368	0.19422
C	-0.69791	-2.44368	-0.19424
C	-1.31677	-3.70952	-0.47651
C	1.40558	-1.23276	0.25052
C	0.72723	0.00000	0.00001
C	-0.72723	0.00000	0.00000
C	-1.40558	-1.23276	-0.25052
C	1.40558	1.23276	-0.25051
C	0.69791	2.44368	-0.19422
C	-0.69792	2.44368	0.19424
C	-1.40559	1.23276	0.25053
C	1.31677	3.70953	-0.47647
C	0.66281	4.88613	-0.25985
C	-0.66282	4.88612	0.25989
C	-1.31678	3.70952	0.47651
C	-2.82069	-1.25822	-0.73805
C	-2.82070	1.25822	0.73805
C	2.82069	-1.25822	0.73804
C	-3.09362	-0.79555	-2.03196
C	-4.37720	-0.87791	-2.56549
C	-5.41395	-1.42201	-1.81092
C	-5.15548	-1.88613	-0.52243
C	-3.86967	-1.81127	0.00560
C	-3.86967	1.81129	-0.00560
C	-5.15548	1.88614	0.52243
C	-5.41395	1.42200	1.81091
C	-4.37721	0.87788	2.56549
C	-3.09363	0.79553	2.03195
C	3.09363	-0.79557	2.03195
C	4.37721	-0.87793	2.56548
C	5.41396	-1.42202	1.81089

C	5.15548	-1.88611	0.52239
C	3.86967	-1.81126	-0.00563
C	2.82069	1.25822	-0.73803
C	3.86966	1.81130	0.00561
C	5.15547	1.88616	-0.52241
C	5.41395	1.42202	-1.81089
C	4.37721	0.87789	-2.56546
C	3.09363	0.79553	-2.03193
H	-1.15791	-5.82863	-0.47159
H	1.15791	-5.82863	0.47153
H	2.33045	-3.72174	0.85387
H	-2.33045	-3.72173	-0.85391
H	2.33045	3.72174	-0.85387
H	1.15791	5.82864	-0.47153
H	-1.15792	5.82863	0.47158
H	-2.33046	3.72173	0.85390
H	-2.28705	-0.37755	-2.62582
H	-4.56554	-0.52040	-3.57323
H	-6.41590	-1.48541	-2.22361
H	-5.95777	-2.30693	0.07547
H	-3.67638	-2.17144	1.01006
H	-3.67638	2.17147	-1.01004
H	-5.95777	2.30696	-0.07546
H	-6.41591	1.48540	2.22361
H	-4.56556	0.52036	3.57322
H	-2.28706	0.37751	2.62581
H	2.28706	-0.37759	2.62582
H	4.56555	-0.52044	3.57322
H	6.41591	-1.48542	2.22358
H	5.95778	-2.30690	-0.07552
H	3.67638	-2.17141	-1.01009
H	3.67637	2.17149	1.01006
H	5.95776	2.30698	0.07548
H	6.41591	1.48541	-2.22358
H	4.56556	0.52036	-3.57319
H	2.28706	0.37751	-2.62579

Rubrene neutral (E = – 1617.32953669 Hartree): planar (C_{2h})

C	-0.00000	-0.00000	0.73723
C	-1.00598	0.74653	1.42906
C	-2.07751	1.32753	0.72323
C	-3.15091	2.00825	1.39853
C	-4.16674	2.61008	0.71196
C	-0.88850	1.12775	2.87765
C	-1.66775	0.54308	3.88589
C	-1.60471	1.01098	5.19830
C	-0.76992	2.08166	5.52481
C	0.00000	2.68196	4.52774
C	-0.06323	2.21104	3.21595
H	-3.15369	2.03005	2.48058
H	-4.97217	3.09962	1.25303
H	-2.31884	-0.29027	3.63915
H	-2.20960	0.53720	5.96701
H	-0.72408	2.44729	6.54729
H	0.64514	3.52342	4.76796
H	0.52748	2.68913	2.43890
C	1.00598	-0.74653	1.42906
C	2.07751	-1.32753	0.72323
C	3.15091	-2.00825	1.39853
C	4.16674	-2.61008	0.71196
C	0.88850	-1.12775	2.87765
C	1.66775	-0.54308	3.88589
C	1.60471	-1.01098	5.19830
C	0.76992	-2.08166	5.52481
C	-0.00000	-2.68196	4.52774
C	0.06323	-2.21104	3.21595
H	3.15369	-2.03005	2.48058
H	4.97217	-3.09962	1.25303
H	2.31884	0.29027	3.63915
H	2.20960	-0.53720	5.96701
H	0.72408	-2.44729	6.54729
H	-0.64514	-3.52342	4.76796
H	-0.52748	-2.68913	2.43890

C	0.00000	0.00000	-0.73717
C	1.00621	-0.74628	-1.42895
C	2.07767	-1.32730	-0.72301
C	3.15132	-2.00767	-1.39829
C	4.16696	-2.60976	-0.71168
C	0.88928	-1.12720	-2.87767
C	1.66823	-0.54163	-3.88561
C	1.60583	-1.00926	-5.19815
C	0.77201	-2.08058	-5.52507
C	0.00242	-2.68179	-4.52829
C	0.06499	-2.21111	-3.21639
H	3.15442	-2.02900	-2.48034
H	4.97258	-3.09901	-1.25271
H	2.31858	0.29220	-3.63855
H	2.21047	-0.53480	-5.96663
H	0.72668	-2.44600	-6.54765
H	-0.64196	-3.52373	-4.76884
H	-0.52546	-2.68985	-2.43954
C	-1.00621	0.74628	-1.42895
C	-2.07767	1.32730	-0.72301
C	-3.15132	2.00767	-1.39829
C	-4.16696	2.60976	-0.71168
C	-0.88928	1.12720	-2.87767
C	-1.66823	0.54163	-3.88561
C	-1.60583	1.00926	-5.19815
C	-0.77201	2.08058	-5.52507
C	-0.00242	2.68179	-4.52829
C	-0.06499	2.21111	-3.21639
H	-3.15442	2.02900	-2.48034
H	-4.97258	3.09901	-1.25271
H	-2.31858	-0.29220	-3.63855
H	-2.21047	0.53480	-5.96663
H	-0.72668	2.44600	-6.54765
H	0.64196	3.52373	-4.76884
H	0.52546	2.68985	-2.43954

(Rubrene)$^-$ anion (E = – 1617.70184762 Hartree): twisted (D_2)

C	0.65232	4.91750	-0.26368
C	-0.65262	4.91749	0.26338
C	-1.30198	3.72131	0.48520
C	-0.69517	2.46477	0.19936
C	0.69500	2.46480	-0.19935
C	1.30175	3.72133	-0.48535
C	-1.40010	1.22832	0.27250
C	-0.72955	-0.00003	0.00016
C	0.72959	0.00003	0.00016
C	1.40004	1.22839	-0.27233
C	-1.40000	-1.22839	-0.27232
C	-0.69497	-2.46480	-0.19936
C	0.69520	-2.46478	0.19936
C	1.40014	-1.22832	0.27251
C	-1.30172	-3.72133	-0.48535
C	-0.65229	-4.91750	-0.26368
C	0.65264	-4.91749	0.26339
C	1.30201	-3.72131	0.48521
C	2.79523	1.22930	-0.80317
C	2.79535	-1.22917	0.80329
C	-2.79534	1.22914	0.80322
C	3.05704	0.63324	-2.04739
C	4.32371	0.67839	-2.62258
C	5.37080	1.32424	-1.96664
C	5.13234	1.91846	-0.72875
C	3.86308	1.87136	-0.15791
C	3.86333	-1.87059	0.15762
C	5.13263	-1.91769	0.72837
C	5.37100	-1.32411	1.96658
C	4.32377	-0.67889	2.62294
C	3.05708	-0.63372	2.04782
C	-3.05712	0.63363	2.04770
C	-4.32385	0.67877	2.62276
C	-5.37105	1.32400	1.96637

C	-5.13262	1.91763	0.72820
C	-3.86329	1.87058	0.15752
C	-2.79522	-1.22928	-0.80310
C	-3.86306	-1.87127	-0.15777
C	-5.13235	-1.91834	-0.72854
C	-5.37085	-1.32414	-1.96642
C	-4.32377	-0.67833	-2.62244
C	-3.05707	-0.63322	-2.04731
H	1.15539	5.85555	-0.48485
H	-1.15575	5.85554	0.48444
H	-2.31294	3.73639	0.87303
H	2.31272	3.73642	-0.87316
H	-2.31269	-3.73642	-0.87316
H	-1.15538	-5.85555	-0.48485
H	1.15577	-5.85555	0.48446
H	2.31296	-3.73640	0.87304
H	2.24444	0.13369	-2.56514
H	4.49205	0.21219	-3.59004
H	6.36095	1.36038	-2.41264
H	5.94107	2.41487	-0.19889
H	3.69175	2.32937	0.81025
H	3.69208	-2.32809	-0.81080
H	5.94146	-2.41359	0.19819
H	6.36118	-1.36025	2.41252
H	4.49204	-0.21319	3.59065
H	2.24438	-0.13466	2.56589
H	-2.24445	0.13456	2.56579
H	-4.49217	0.21302	3.59044
H	-6.36126	1.36011	2.41226
H	-5.94143	2.41355	0.19800
H	-3.69200	2.32812	-0.81087
H	-3.69170	-2.32926	0.81040
H	-5.94107	-2.41470	-0.19862
H	-6.36103	-1.36024	-2.41237
H	-4.49215	-0.21214	-3.58989
H	-2.24449	-0.13371	-2.56512

(Rubrene)$^-$ anion (E = – 1617.69418346 Hartree): planar (C_{2h})

C	-0.00000	0.00000	0.73731
C	1.24770	0.09312	1.42064
C	2.45198	0.40107	0.72117
C	3.69210	0.62194	1.38681
C	4.86531	0.86181	0.70272
C	1.39861	-0.34293	2.84620
C	1.67521	0.53356	3.90419
C	1.90650	0.06151	5.19402
C	1.87128	-1.30588	5.46018
C	1.60106	-2.19415	4.42065
C	1.37103	-1.71594	3.13331
H	3.71628	0.59521	2.46849
H	5.78647	1.03636	1.25324
H	1.69311	1.60064	3.71049
H	2.10634	0.76672	5.99628
H	2.05077	-1.67451	6.46648
H	1.57607	-3.26422	4.61063
H	1.17012	-2.41140	2.32445
C	-1.24770	-0.09312	1.42064
C	-2.45198	-0.40107	0.72117
C	-3.69210	-0.62194	1.38681
C	-4.86531	-0.86181	0.70272
C	-1.39861	0.34293	2.84620
C	-1.67521	-0.53356	3.90419
C	-1.90650	-0.06151	5.19402
C	-1.87128	1.30588	5.46018
C	-1.60106	2.19415	4.42065
C	-1.37103	1.71594	3.13331
H	-3.71628	-0.59521	2.46849
H	-5.78647	-1.03636	1.25324
H	-1.69311	-1.60064	3.71049
H	-2.10634	-0.76672	5.99628
H	-2.05077	1.67451	6.46648
H	-1.57607	3.26422	4.61063
H	-1.17012	2.41140	2.32445

C	-0.00000	0.00000	-0.73731
C	-1.24770	-0.09312	-1.42064
C	-2.45198	-0.40107	-0.72117
C	-3.69210	-0.62194	-1.38681
C	-4.86531	-0.86181	-0.70272
C	-1.39861	0.34293	-2.84620
C	-1.67521	-0.53356	-3.90419
C	-1.90650	-0.06151	-5.19402
C	-1.87128	1.30588	-5.46018
C	-1.60106	2.19415	-4.42065
C	-1.37103	1.71594	-3.13331
H	-3.71628	-0.59521	-2.46849
H	-5.78647	-1.03636	-1.25324
H	-1.69311	-1.60064	-3.71049
H	-2.10634	-0.76672	-5.99628
H	-2.05077	1.67451	-6.46648
H	-1.57607	3.26422	-4.61063
H	-1.17012	2.41140	-2.32445
C	1.24770	0.09312	-1.42064
C	2.45198	0.40107	-0.72117
C	3.69210	0.62194	-1.38681
C	4.86531	0.86181	-0.70272
C	1.39861	-0.34293	-2.84620
C	1.67521	0.53356	-3.90419
C	1.90650	0.06151	-5.19402
C	1.87128	-1.30588	-5.46018
C	1.60106	-2.19415	-4.42065
C	1.37103	-1.71594	-3.13331
H	3.71628	0.59521	-2.46849
H	5.78647	1.03636	-1.25324
H	1.69311	1.60064	-3.71049
H	2.10634	0.76672	-5.99628
H	2.05077	-1.67451	-6.46648
H	1.57607	-3.26422	-4.61063
H	1.17012	-2.41140	-2.32445

References

1) Sato, N.; Seki, K.; Inokuchi, H. Polarization Energies of Organic Solids Determined by Ultraviolet Photoelectron Spectroscopy. *J. Chem. Soc. Faraday Transactions 2*. **1981**, *77*, 1621-1633.

2) Ding, H.; Gao, Y. Rubrene: Electronic Structure, Interface Energy Level Alignment, and Growth Dynamics. *Proc. of SPIE* **2010**, *7778*, 77780J.

3) Nakayama, Y.; Uragami, Y.; Machida, S.; Koswattage, K. R.; Yoshimura D.; Setoyama, H.; Okajima, T.; Mase, K.; Ishii, H. Full Picture of Valence Band Structure of Rubrene Single Crystals Probed by Angle-Resolved and Excitation-Energy-Dependent Photoelectron Spectroscopy. *Appl. Phys. Express* **2012**, *5*, 111601.

4) Sutton, C.; Tummala, N. R.; Beljonne, D.; Brédas, J.-L. Singlet Fission in Rubrene Derivatives: Impact of Molecular Packing. *Chem. Mater.* **2017**, *29*, 2777−2787.

5) Yassar, A.; Camposeo, A.; Polo, M.; Pisignano, D. Optical Response and Emission Waveguiding in Rubrene Crystals. *Phys. Rev. B.* **2007**, *75*, 245416.

6) Irkhin, P.; Ryasnyanskiy, A.; Koehler, M.; Biaggio, I. Absorption and Photoluminescence Spectroscopy of Rubrene Single Crystals. *Phys. Rev. B.* **2012**, *86*, 085143.

7) Iimori, T.; Ito, R.; Ohta, N.; Nakano, H. Stark Spectroscopy of Rubrene. I. Electroabsorption Spectroscopy and Molecular Parameters. *J. Phys. Chem. A.* **2016**, *120*, 4307−4313.

8) Herkstroeter, W. G.; Merkel, P. B. The Triplet State Energies of Rubrene and Diphenylisobenzofuran. *J. Photochem.* **1981**, *16*, 331−341.

9) Ma, L.; Zhang, K.; Kloc, C.; Sun, H.; Michel-Beyerle, M. E.; Gurzadyan, G. G. Singlet Fission in Rubrene Single Crystal: Direct Observation by Femtosecond Pump-Probe Spectroscopy. *Phys. Chem. Chem. Phys.* **2012**, *14*, 8307−8312.

10) Jankus, V.; Snedden, E. W.; Bright, D. W.; Arac, E.; Dai, D.; Monkman, A. P. Competition between Polaron Pair Formation and Singlet Fission Observed in Amorphous Rubrene Films. *Phys. Rev. B.* **2013**, *87*, 224202.