Supporting Information

Time-gated triplet-state optical spectroscopy to decipher organic luminophores embedded in rigid matrices

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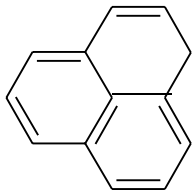
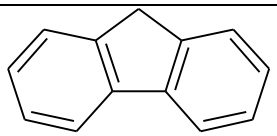
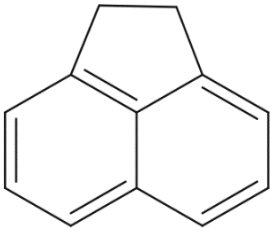
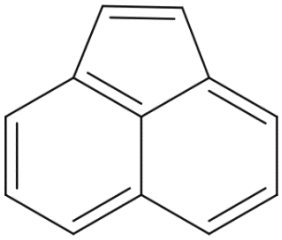
Supplementary contents

Table S1. S-S transitions and oscillator strengths, and S-T transitions computed by TD-DFT calculations with B3LYP[1] exchange-correlation potential (20 % Hartree-Fock) and TZ2P basis sets throughout for a selection of poly-aromatic/cyclic molecules (cf. Table S1 of Angew. Chem. Int. Ed. 2017, 56, 13995-13998). The first four models were selected by ^{13}C and ^{1}H ENDOR experiments, and the other models are here considered for illustrative purposes. Experiment: Exc($S_0 \rightarrow S_1$) = 3.7 eV, Exc($S_0 \rightarrow S_2$) = 4.9 eV, and PhL($T_1 \rightarrow S_0$) = 2.8 eV.

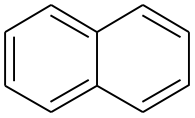
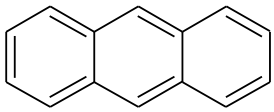
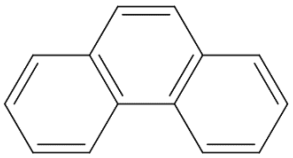
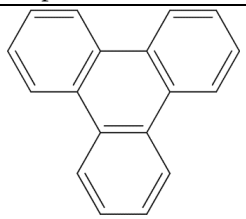
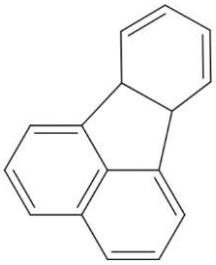
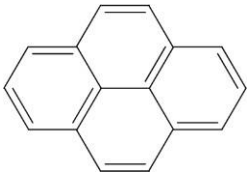
Molecular models	S-S Transitions (eV)	S-S Oscillator strength	S-T Transitions (eV)	Selected by ENDOR
 Phenalene	**3.68** 4.16 **4.99** 5.24 5.43	0.153 0.008 0.100 0.001 0.329	**2.38** 3.53 3.72 4.06 4.44	yes
 fluorene	4.53 4.75* 5.56 5.82 6.49	0.147 0.314 0.013 0.240 0.816	3.25 4.07 (x 2) 4.36 (x 2) 4.74 4.84	yes
 acenaphthene[2]	4.27* 5.42 5.79 5.98 6.14	0.090 0.023 0.954 0.162 0.006	2.85 3.85 4.22 4.36 4.46	yes
 acenaphthylene[3]	3.11 3.89* 4.20 4.92 5.66	0.005 0.098* 0.094 0.022 0.436	2.29 2.61 3.36 4.19 4.53	yes
 benzene[4]	7.14* 7.36	1.254* 0.107	4.03* 4.77*	no

[1] A. D. Becke, *Journal of Chemical Physics*, 1993, **98**, 1372-1377 ; C. T. Lee, W. T. Yang and R. G. Parr, *Physical Review B*, 1988, **37**, 785-789.

[2] Experimental values : S-S → 4.29. Source : B. Dick & G. Hohlneicher, Chem. Phys. Lett. 1981, 84, 471-478.

[3] Experimental values (n-pentane, 77 K): S-S → 2.66 (0.004), 3.66 (0.165), 3.85, 4.51 (0.005). Source : J. Banisaukas *et al.*, J. Phys. Chem. A 2003, 107, 782-793.

[4] Experimental values (gas-phase): S-S → 6.94 (0.80); S-T → 3.94, 4.76. Source : H. H. Heinze *et al.*, J. Chem. Phys., Vol. 113, 2088-2099.

 naphtalene[5]	4.42* 5.98* 6.16* 6.64 7.24	0.059 1.131 0.194 0.020 0.059	2.91 4.02 4.27 4.35 4.49	No
 anthracene[6]	3.25* 5.23* 5.82 6.01 6.81	0.056 2.034 0.085 0.016 0.301	1.97 3.43 3.53 3.72 4.24	No
 phenanthrene[7]	4.25* 4.74 4.95 5.11 5.17	0.062* 0.108 0.626 0.019 0.100	2.94* 3.53 3.63 3.86 4.07	No
 triphenylene[8]	4.31 4.76* 4.98 5.70 6.07	0.005 0.784 0.705 0.012 0.272	3.05* 3.56 3.70 3.85 4.24	no
 fluoranthene	4.14 4.32 4.59 5.42 5.66 5.83	0.037 0.071 0.038 0.037 0.023 0.559	2.69 2.86 3.86 3.98 4.13	no
 pyrene[9]	3.71* 4.60* 5.43	0.267 0.267 0.806	2.29 3.47 3.61	no

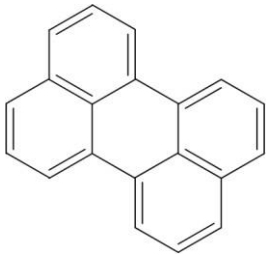
[5] Experimental values (gas-phase): S-S → 4.45 (0.102/p), 5.89 (1.3/β), 6.14 (0.3). Source : G. Malloci *et al.*, Chemical Physics 340 (2007) 43–58.

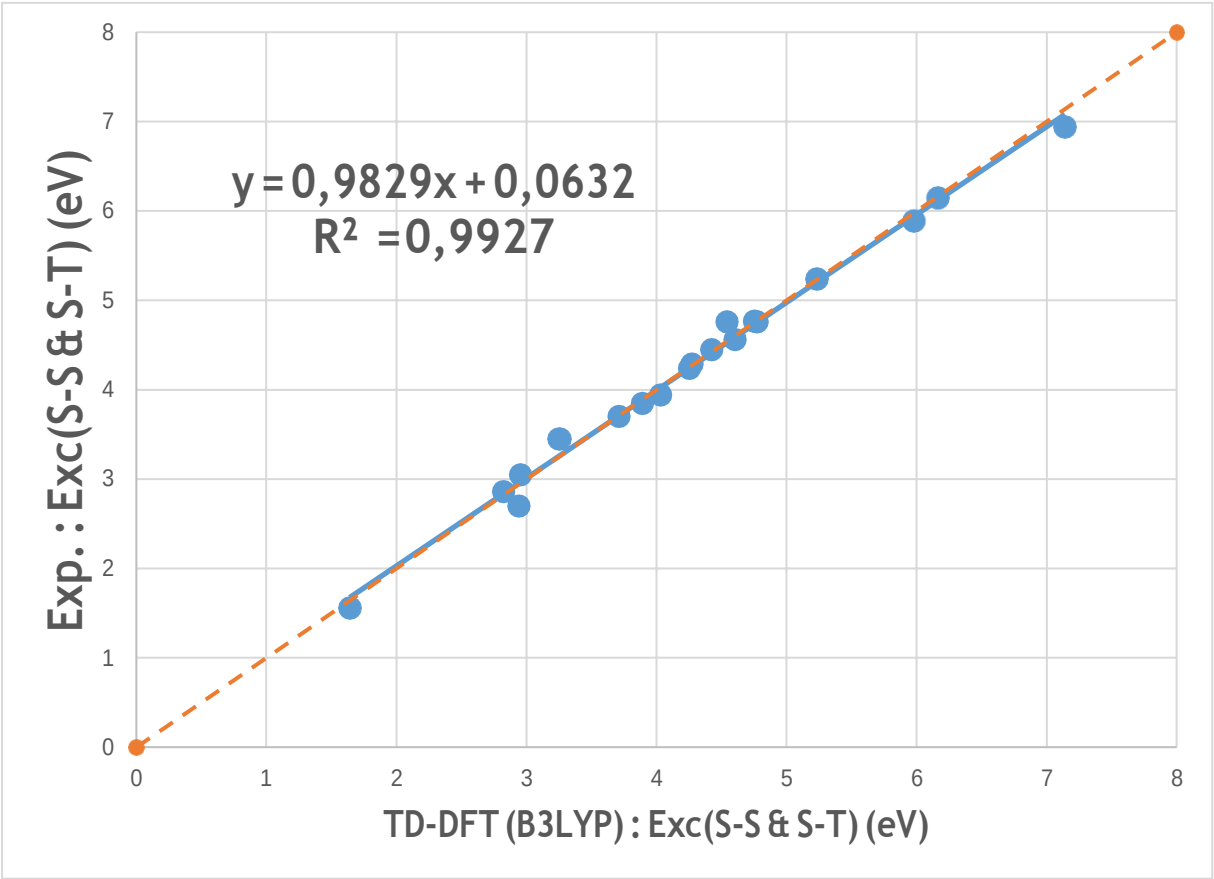
[6] Experimental values (gas-phase): S-S → 3.45 (p), 5.24 (β). Source : G. Malloci *et al.*, Chemical Physics 340 (2007) 43–58.

[7] Experimental values (gas-phase): S-S → 4.24 (p); S-T → 2.70. Source : M. Parac *et al.*, Chemical Physics 292 (2003) 11–21.

[8] Experimental values (gas-phase): S-S → 3.89, 4.54; S-T → 2.95. Source : M. Parac *et al.*, Chemical Physics 292 (2003) 11–21.

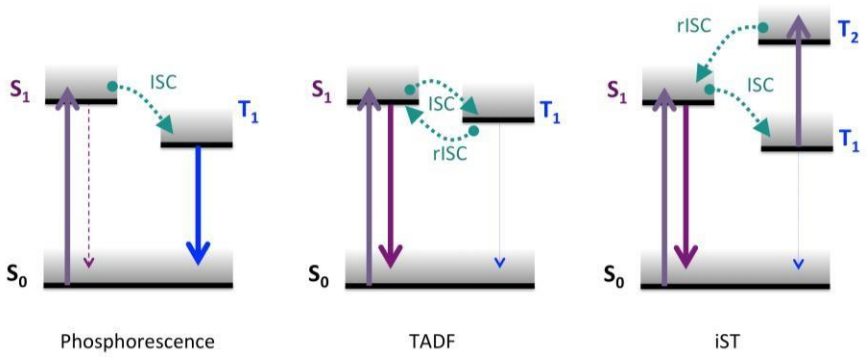
[9] (a) Experimental values (water solution ; w = weak, s = strong): S-S → 232^{w} (5.34 eV), 242^{s} (5.12 eV), 252^{w} (4.92 eV), 260^{w} (4.77 eV), 272^{s} (4.56 eV)*, 308^{w} (4.03 eV), 320^{s} (3.88 eV) and 336^{s} (3.69 eV)* nm. Source : J. Gališinová *et al.*, Acta Fac. Pharm. Univ. Comen. LX, 2013, (1), p. 1-6. (b) Experimental values (gas-phase): S-S → 3.53, 3.71; S-T → 2.08. Source : M. Parac *et al.*, Chemical Physics 292 (2003) 11–21.

 perylene[10]	2.82* 4.02 4.85 5.36 5.54	0.345 0.008 0.313 0.010 0.117	1.64* 3.12 3.24 3.37 3.59	no



Plot of some of the computed TD-DFT S-S and S-T transitions (marked by * in the previous table) as a function of experimental data (when available). Blue continuous line: correlation line. Orange plotted line: unity line. Standard deviation: $\sigma = 0.11$ eV (18 points).

[10] (a) Experimental values (acetonitrile solution): S-S → 386 (3.21 eV), 406 (3.05 eV), 433 (2.86 eV)*, nm. Source: L. Lin *et al.*, J. Mater. Chem. A, 2015, 3, 12845–12851. (b) Experimental values (gas-phase): S-S → 2.85*; S-T → 1.56*. Source: M. Parac *et al.*, Chemical Physics 292 (2003) 11–21.



Scheme S1. Schematics of phosphorescence, thermally-assisted delayed fluorescence (TADF) and inverse singlet-triplet (iST) mechanisms leading to afterglow luminescence in molecular systems.

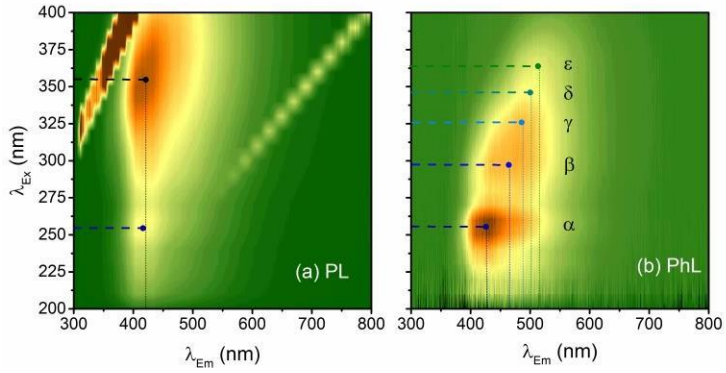


Figure S1. Steady-state (a) and time-gated (b) luminescence contour maps of SG-500 a-YAB powder. In (a), the diagonal features are excitation pump signals. In time-gated plot (b), data represent the phosphorescence signals at 1 s after ceasing the excitation.

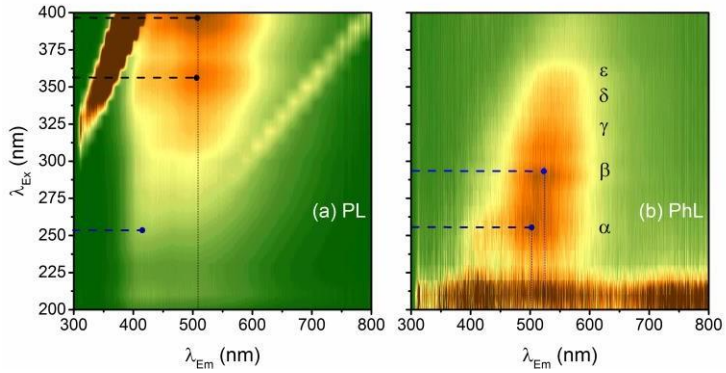


Figure S2. Steady-state (a) and time-gated (b) luminescence contour maps of SG-570 a-YAB powder. In (a), the diagonal features are excitation pump signals. In time-gated plot (b), data represent the phosphorescence signals at 0.5 s after ceasing the excitation.

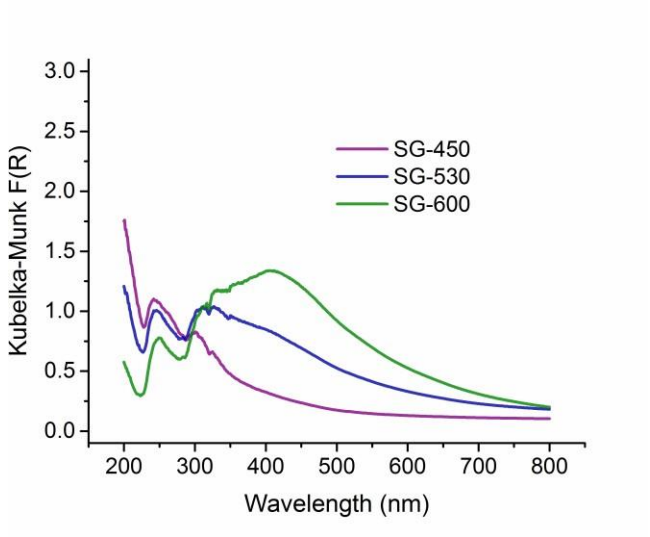


Figure S3. Diffuse reflectance spectra of a-YAB powders calcined at different temperatures.

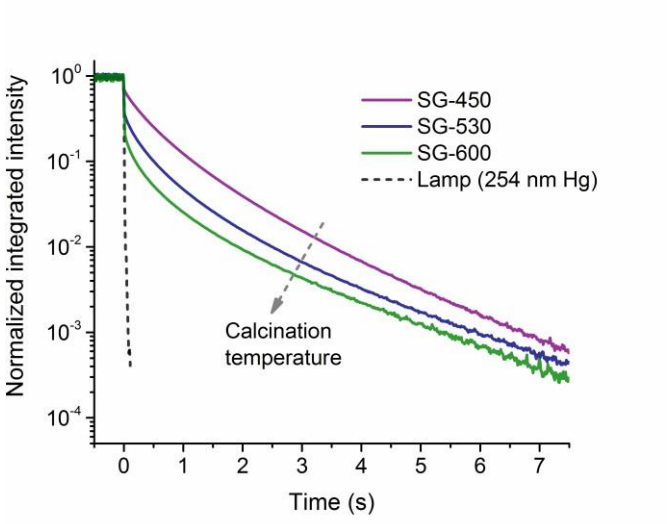


Figure S4. PL normalized phosphorescence afterglow of a-YAB powders calcined at different temperatures. The powders were excited by 254 nm Hg vapor lamp for 1 minute before ceasing the excitation. The lamp decay is also presented in the figure showing the instrument response function after ceasing the lamp excitation. The relative afterglow intensity falls monotonously for samples calcined at higher temperature.