Electronic Supplementary Material (ESI) for Molecular Systems Design & Engineering.

Supporting information

Reversible Switching of Solid-State Luminescence by Heat-Induced Interconversion of Molecular Packing

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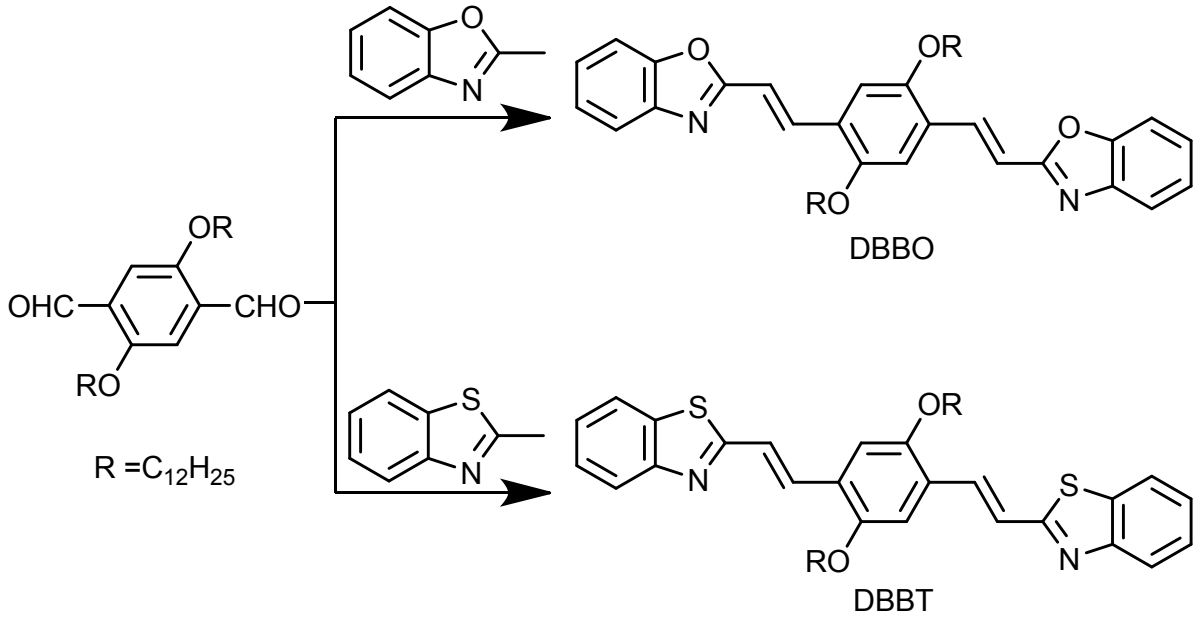

Scheme S1: Synthesis of **DBBO** and **DBBT**; *Reagents and conditions*: *t*-BuOK, 0 °C, dry THF, 2h

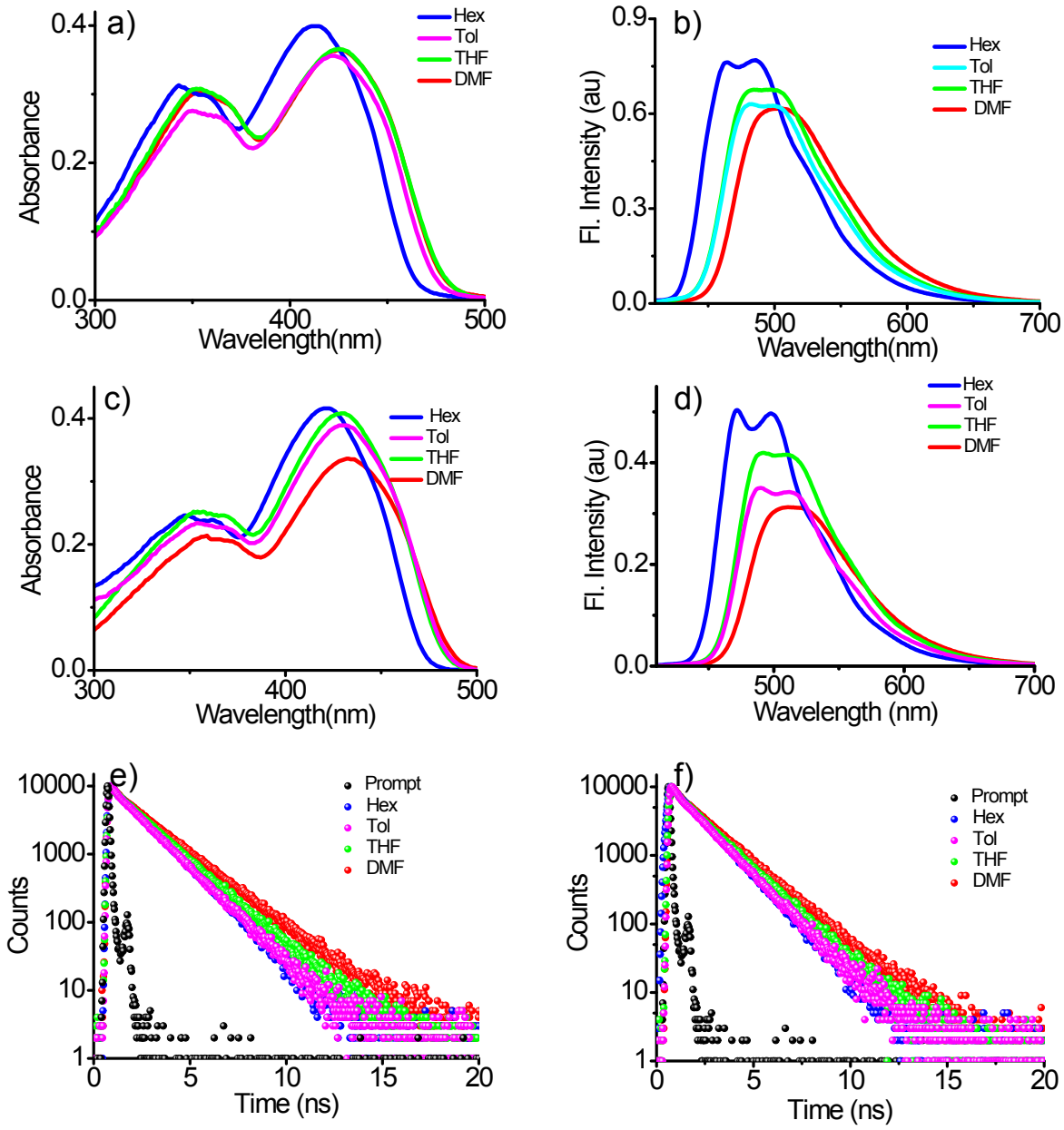

Fig.S1: **Fig.S1:** Absorption spectra of (a) **DBBO** and (b) **DBBT**; emission spectra of (c) **DBBO** and (d) **DBBT**; time-resolved fluorescence decay profile of (e) **DBBO** and (f) **DBBT** recorded in various solvents.

Table S1: Absorption maximum, extinction coefficient (ε), emission maximum, fluorescence quantum yield (Φ_f) and average fluorescence lifetime (τ_f) of **DBBO** and **DBBT** in various solvents.

Compound	Solvent	λ_{abs} (nm)	$\varepsilon \times 10^5$ (cm^{-1})	λ_{em} (nm)	Φ_f	τ_f (ns)
DBBO	Hexane	354, 413	0.29,0.40	462,486	0.77	1.54
	Toluene	352, 422	0.27,0.36	484,500	0.78	1.55
	THF	352,426	0.30,0.37	481,500	0.82	1.73
	DMF	352,426	0.30,0.37	504	0.79	2.00
DBBT	Hexane	360,421	0.24,0.42	471,497	0.80	1.47
	Toluene	359,429	0.25,0.41	490,511	0.84	1.50
	THF	361,430	0.23,0.39	488,514	0.88	1.62
	DMF	362,432	0.21,0.33	514	0.84	1.82

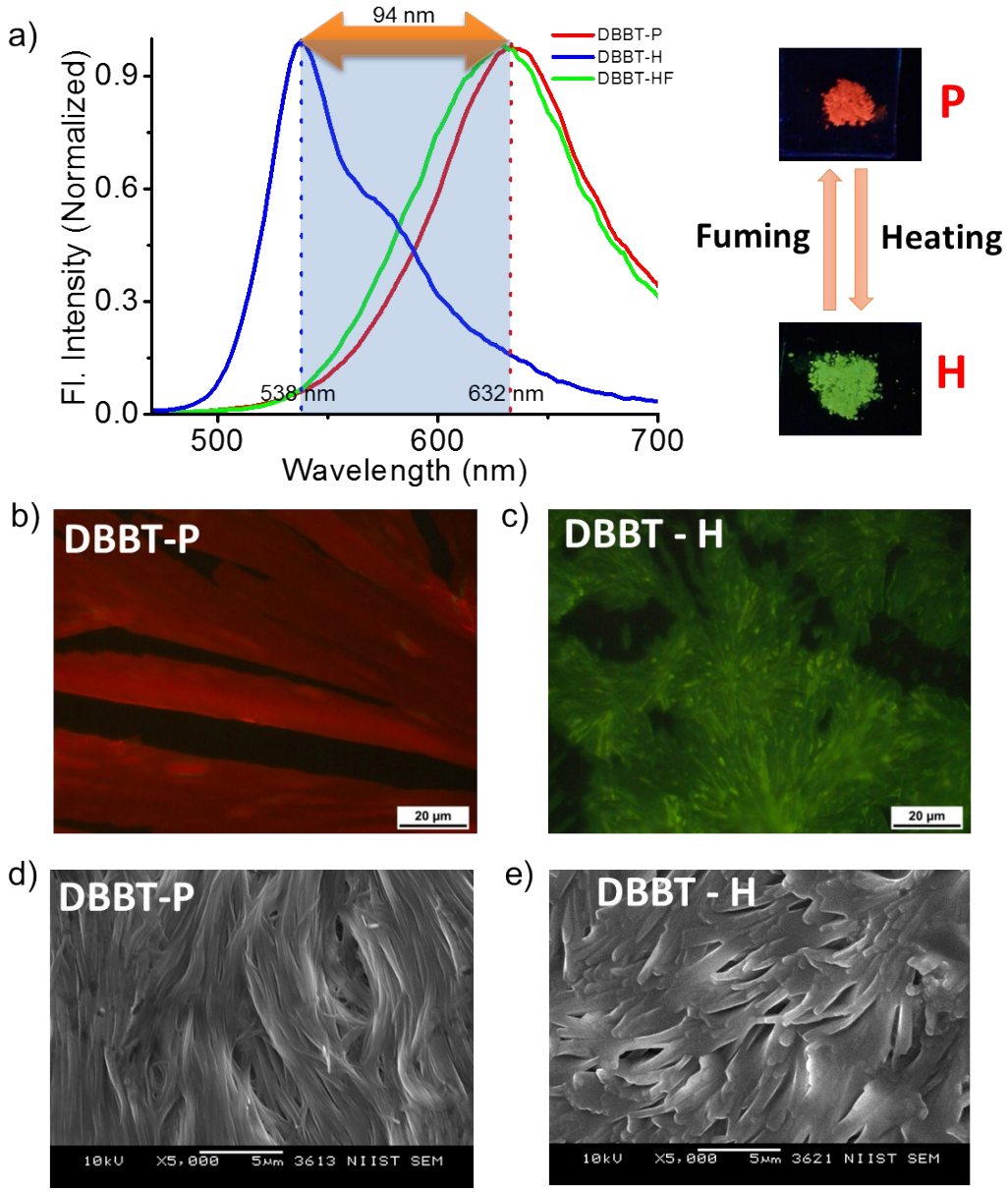

Fig.S2: (a) Photoluminescence spectra of **DBBT** under different conditions; P – pristine powder sample, H – sample heated at 80 °C followed by air cooled to room temperature and HF – sample H on fuming with dichloromethane. Photographs of the pristine and heated samples under 365 nm UV light are shown at the right side. Fluorescence microscopy images of the (b) pristine and (c) heated samples of **DBBT** under excitation by UV source. FE-SEM images of self-assembled structures of (d) pristine and (e) heated samples of **DBBT**.

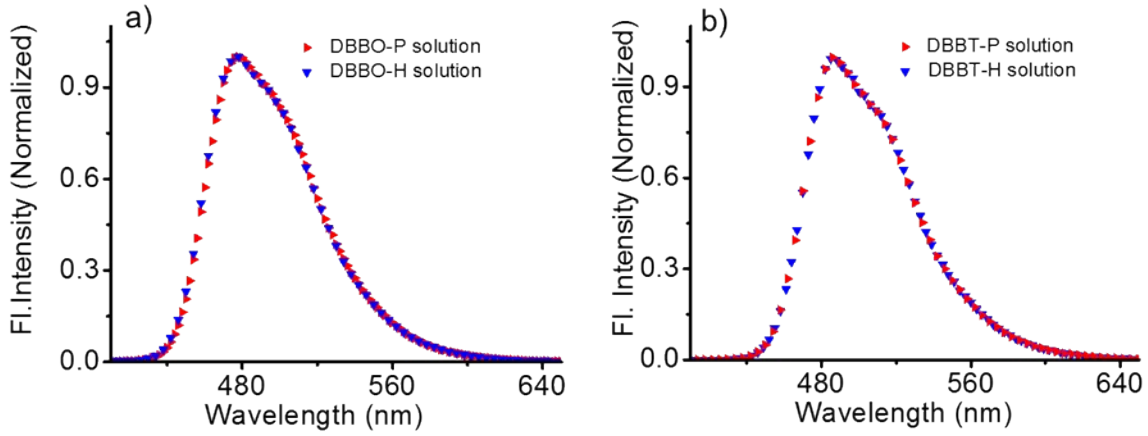

Fig. S3: Emission spectra taken for P-state and H-state powders dissolved in THF of a) **DBBO** and b) **DBBT**

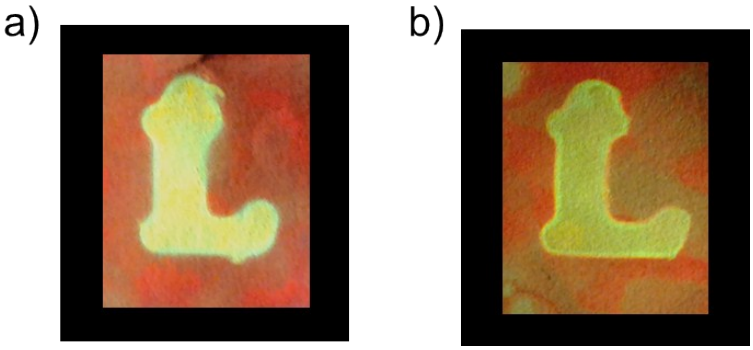

Fig.S4: Fluorescent image recorded on a filter paper coated with a) **DBBO** and b) **DBBT** by keeping a hot metallic letter 'L', which was then removed, under 365 nm UV lamp.

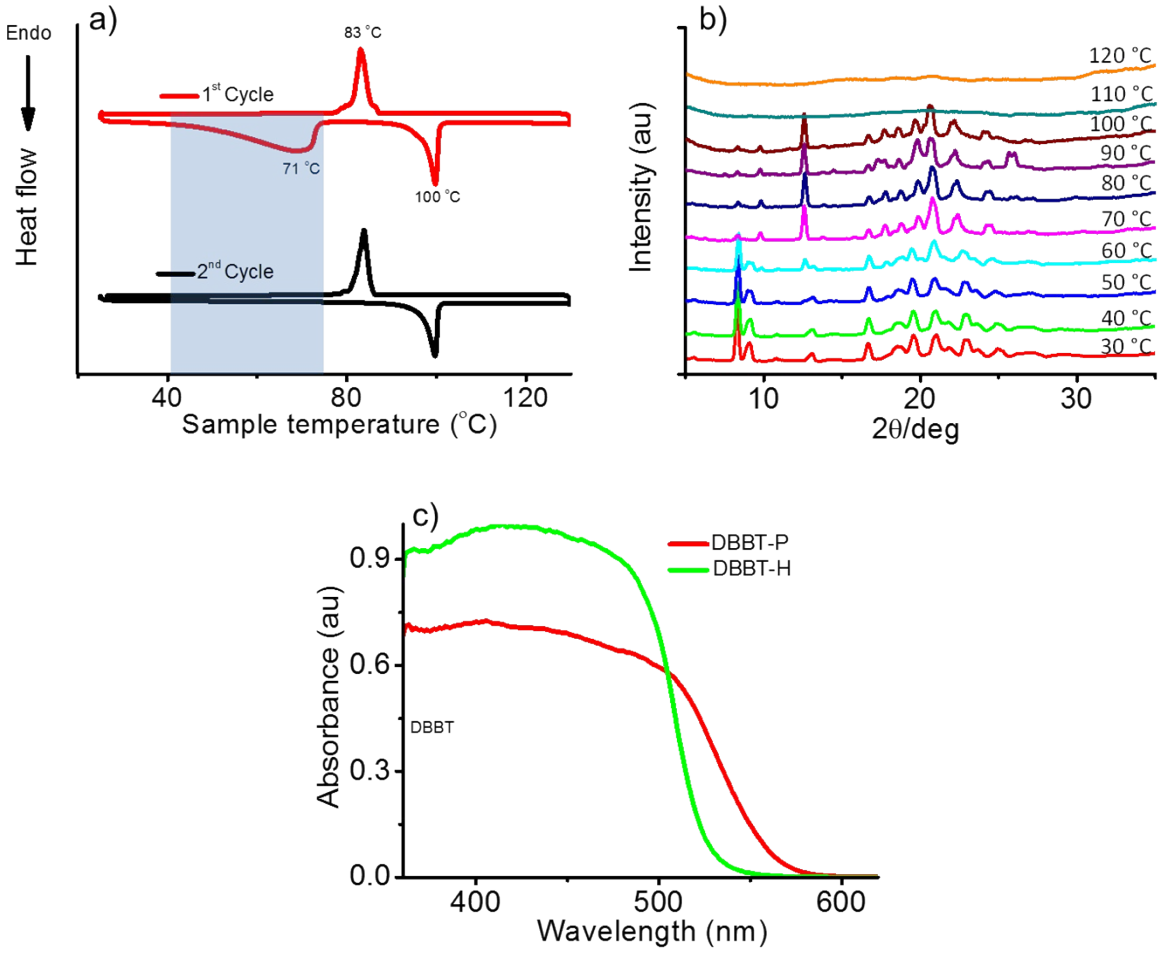

Fig.S5: a) First and second heating cycle of DSC thermogram, b) temperature dependent XRD pattern and c) solid-state absorption spectra of P-form and H-form of **DBBT**.

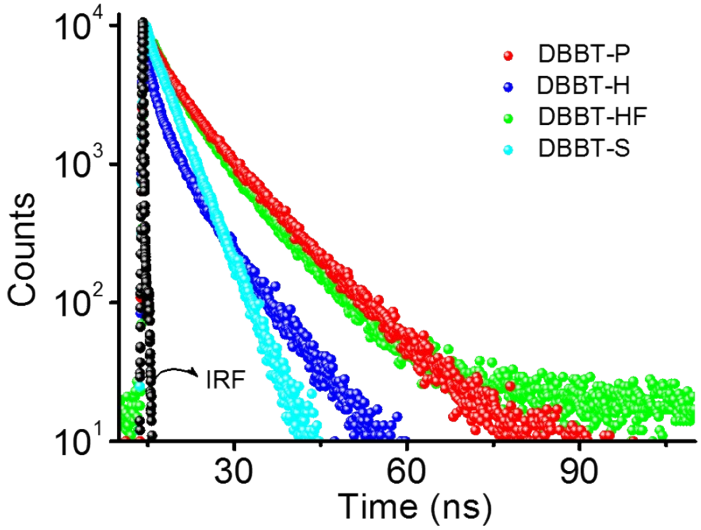

Fig.S6: Time-resolved fluorescence decay profile of **DBBT** at different states P – Pristine powder sample, H – heated sample and HF – H powder on fuming with dichloromethane; S – Molecularly dissolved state (IRF – Instrument response factor).

Table S2. Average fluorescence life time of **DBBO** and **DBBT** at different states

Compound at different states	P (ns)	H (ns)	HF (ns)	M (ns)	MD (ns)
DBBO	10.77	6.03	10.27	7.76	1.55
DBBT	6.45	2.22	4.74	3.18	1.50

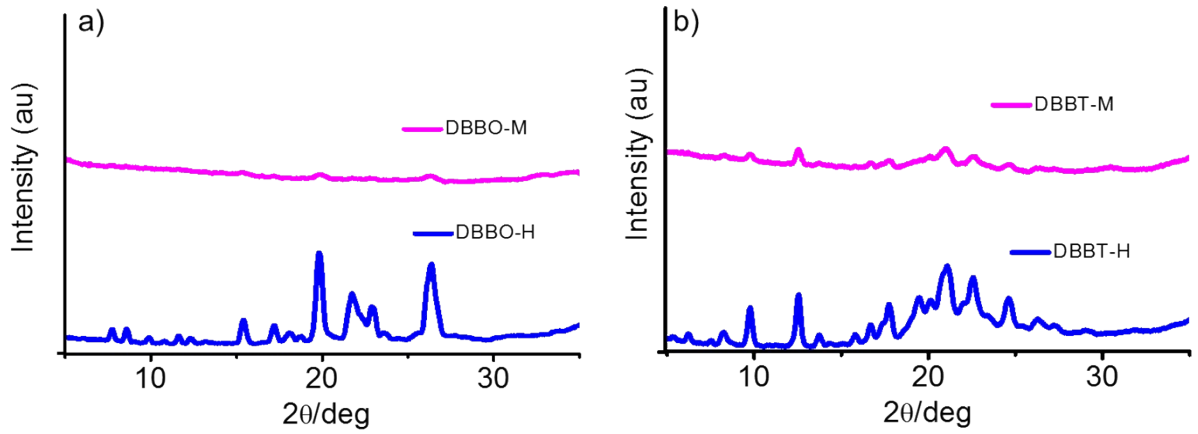

Fig.S7: PXRD pattern under different conditions of a) **DBBO** and b) **DBBT**; H – heated sample and M – ground H sample.