Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Controlled emission colors and singlet–triplet energy gaps of dihydrophenazine-based thermally activated delayed fluorescence emitters

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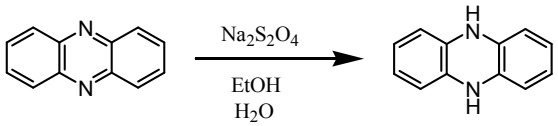
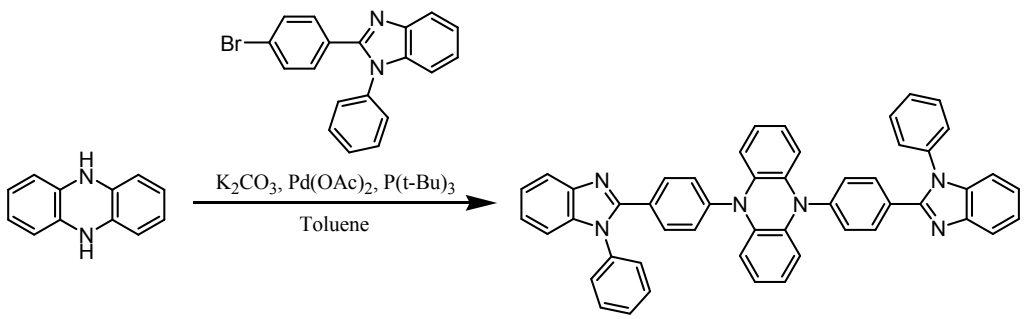
1. Preparation of 5,10-dihydrophenazine[S1]



To a mixture of phenazine (5.00 g, 27.7 mmol) in ethanol (126 mL) was added, with stirring, a solution of sodium dithionate (48.2 g, 277 mmol) in water (504 mL). The mixture was stirred and heated under reflux for 3 h. A white precipitate was collected and washed with water. The collected solids were dried under reduced pressure to afford 5,10-dihydrophenazine (5.02 g, 27.5 mmol). This material was used in the next step without further purification.

[MS]
MALDI-MS *m/z* Calcd for $C_{12}H_{10}N_2$: 182; found: 182.

2. Preparation of 5,10-bis(4-(1-phenyl-1*H*-benzoimidazol-2-yl)phenyl)-5,10-dihydrophenazine (DHPZ-2BI)



To a mixture of 2-(4-bromophenyl)-1-phenyl-1H-benzimidazole (4.22 g, 12.1 mmol) that was synthesized by a reported method,[S2] dihydrophenazine (1.00 g, 5.49 mmol) and potassium carbonate (4.55 g, 32.9 mmol) in toluene (20 mL) was added, with stirring, a solution of palladium(II) acetate (74.1 mg, 0.33 mmol) and tri-*tert*-butylphosphine (244.8 mg, 1.21 mmol) in toluene (20 mL). The mixture was stirred and heated under reflux for 1 day. The cooled mixture was filtered and washed with toluene, ethanol, water, and ethanol sequentially. The resulting yellow solid was dried under reduced pressure to afford DHPZ-2BI (3.83 g, 5.33 mmol). The yield was over 97.0%. The compound was further purified by sublimation under reduced pressure for OLED fabrication.

[NMR]

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.28(d, 8H), 7.36(m, 10H), 7.39(d, 4H), 7.52(m, 8H), 7.89(d, 4H)

[MS]

MALDI-MS *m/z* Calcd for $C_{50}H_{34}N_6$: 719; found: 719.

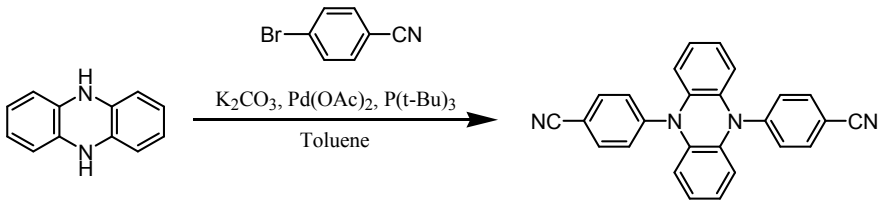
[Elemental analysis]

Calcd for $C_{50}H_{34}N_6$: C, 83.54; H, 4.77; N, 11.69; found: C, 83.62; H, 4.72; N, 11.68.

[Thermal properties]

T_c: 197 °C; T_m: 336 °C; T_d: 484 °C (temperature at 5% weight loss from TGA).

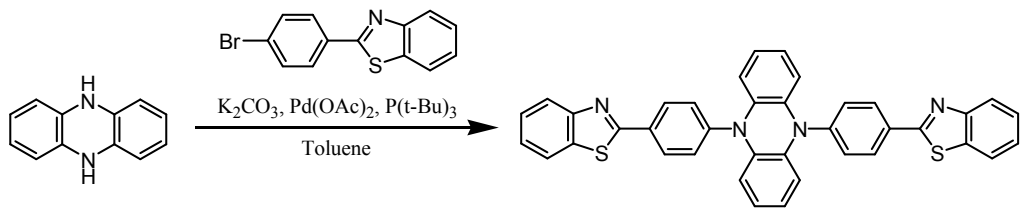
3. Preparation of 4,4′-(phenazine-5,10-diyl)dibenzonitrile (DHPZ-2BN)



To a mixture of 4-bromobenzonitrile (2.20 g, 12.1 mmol), dihydrophenazine (1.00 g, 5.49 mmol) and potassium carbonate (4.55 g, 32.9 mmol) in toluene (20 mL) was added, with stirring, a solution of palladium(II) acetate (74.1 mg, 0.33 mmol) and tri-*tert*-butylphosphine (244.8 mg, 1.21 mmol) in toluene (20 mL). The mixture was stirred and heated under reflux for 1 day. The cooled mixture was partitioned between chloroform and water. The organic layer was separated, and the aqueous layer was extracted with large amounts of chloroform. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. Hexane (20 mL) was added and an orange insoluble solid was separated by filtration. Then, the collected solid was washed with a mixture of hexane and chloroform (2:1) and dried under reduced pressure to give DHPZ-2BN (1.98 g, 5.16 mmol). The yield was over 94%. DHPZ-2BN was further purified by sublimation under reduced pressure for OLED fabrication.

[NMR]
^{1}H NMR ($CDCl_3$, 500 MHz) δ = 5.91(m, 4H), 6.52(m, 4H), 7.50(d, 4H, J = 8.3 Hz), 7.88(d, 4H, J = 8.3 Hz)
[MS]
MALDI-MS *m/z* Calcd for $C_{26}H_{16}N_4$: 384; found: 384.
[Elemental analysis]
Calcd for $C_{26}H_{16}N_4$: C, 81.23; H, 4.20; N, 14.57; found: C, 81.27; H, 4.11; N, 14.49.
[Thermal properties]
T_d: 351 °C (temperature at 5% weight loss from TGA)

4. Preparation of 5,10-bis(4-(benzothiazol-2-yl)phenyl)-5,10-dihydrophenazine (DHPZ-2BTZ)



To a mixture of 2-(4-bromophenyl)benzothiazole (3.51 g, 12.1 mmol), dihydrophenazine (1.00 g, 5.49 mmol) and potassium carbonate (4.55 g, 32.9 mmol) in toluene (20 mL) was added, with stirring, a solution of palladium(II) acetate (74.1 mg, 0.33 mmol) and tri-*tert*-butylphosphine (244.8 mg, 1.21 mmol) in toluene (20 mL). The mixture was stirred and heated under reflux for 1 day. The cooled mixture was filtered and washed with toluene, ethanol, water, and ethanol sequentially. The resulting reddish orange solid was dried under reduced pressure to afford DHPZ-2BTZ (2.77 g, 4.61 mmol). The yield was over 84%. DHPZ-2BTZ was further purified by sublimation under reduced pressure for OLED fabrication.

[NMR]

^{1}H NMR ($CDCl_3$, 400 MHz) δ= 5.78(m, 4H), 6.34(m, 4H), 7.44(t, 2H), 7.54(t, 2H), 7.55(d, 4H), 7.95(d, 2H), 8.11(d, 2H), 8.35(d, 4H)

[MS]

MALDI-MS *m/z* Calcd for $C_{38}H_{24}N_4S_2$: 601; found: 600.

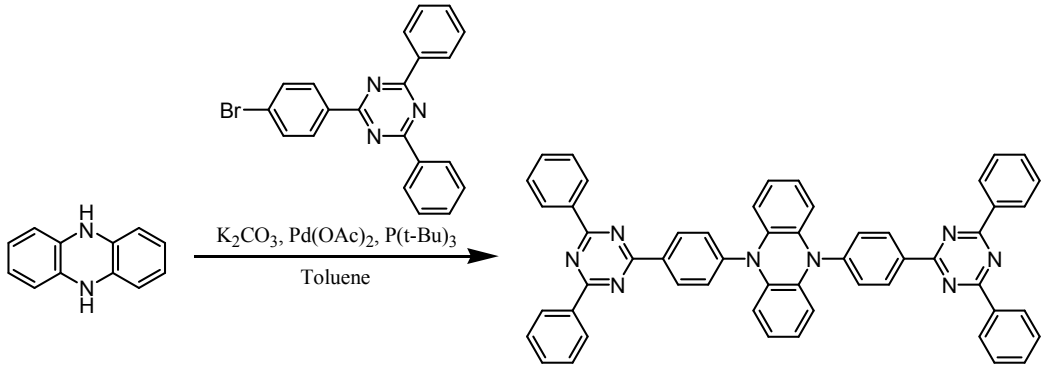
[Elemental analysis]

Calcd for $C_{38}H_{24}N_4S_2$: C, 75.97; H, 4.03; N, 9.33; found: C, 75.91; H, 4.10; N, 9.28.

[Thermal properties]

T_c: 335 °C; T_m: 387 °C; T_d: 461 °C (temperature at 5% weight loss from TGA)

5. Preparation of 5,10-bis(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-5,10-dihydrophenazine (DHPZ-2TRZ)



To a mixture of 2-(4-bromophenyl)-4,6-diphenyl-1,3,5-triazine (4.69 g, 12.1 mmol) that was synthesized by a reported method,[S3] dihydrophenazine (1.00 g, 5.49 mmol) and potassium carbonate (4.55 g, 32.9 mmol) in toluene (20 mL) was added, with stirring, a solution of palladium(II) acetate (74.1 mg, 0.33 mmol) and tri-*tert*-butylphosphine (244.8 mg, 1.21 mmol) in toluene (20 mL). The mixture was stirred and heated under reflux for 1 day. The cooled mixture was partitioned between chloroform and water. The organic layer was separated, and the aqueous layer was extracted with large amounts of chloroform. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. Hexane (20 mL) was added and the resulting red insoluble solid was separated by filtration. Then, the collected solid was washed with a mixture of hexane and chloroform (2:1) and dried under reduced pressure to afford DHPZ-2TRZ (3.72 g, 4.67 mmol). The yield was over 85%. DHPZ-2TRZ was further purified by sublimation under reduced pressure for OLED fabrication.

[NMR]
^{1}H NMR ($CDCl_3$, 500 MHz) δ = 7.64(m, 22H), 8.82(m, 14H)
[MS]
MALDI-MS *m/z* Calcd for $C_{54}H_{36}N_8$: 797; found: 797
[Elemental analysis]
Calcd for $C_{54}H_{36}N_8$: C, 81.39; H, 4.55; N, 14.06; found: C, 81.53; H, 4.49; N, 14.05.
[Thermal properties]
T_d: 496 °C (temperature at 5% weight loss from TGA)

6. Photoluminescence characteristics in toluene solution

Supplementary Table S1. Photoluminescence characteristics of DHPZ-2BI, DHPZ-2BN, DHPZ-2BTZ, and DHPZ-2TRZ (Fig. 1) in toluene solution. τ_p and τ_d are lifetimes of prompt and delayed components, respectively. The delayed components were not observed in air.

Compound	In air			After nitrogen bubbling		
	PLQY (%)	τ_p (ns)	τ_d (μs)	PLQY (%)	τ_p (ns)	τ_d (μs)
DHPZ-2BI	5.7	4.96	–	24.1	6.75	5.71
DHPZ-2BN	3.3	5.02	–	8.4	6.28	1.88
DHPZ-2BTZ	4.7	4.18	–	9.7	6.85	0.24
DHPZ-2TRZ	0.7	1.01	–	2.2	1.08	–

7. Calculated and experimental absorption and emission wavelengths

Supplementary Table S2: Absorption (λ_{ab}) and emission wavelengths (λ_{em}) for DHPZ-2BI, DHPZ-2BN, DHPZ-2BTZ, and DHPZ-2TRZ were computed using time-dependent density functional theory (TD-DFT) at the CAM-B3LYP/cc-pVDZ level of theory. Solvent effects were taken into account by means of the polarizable continuum model.

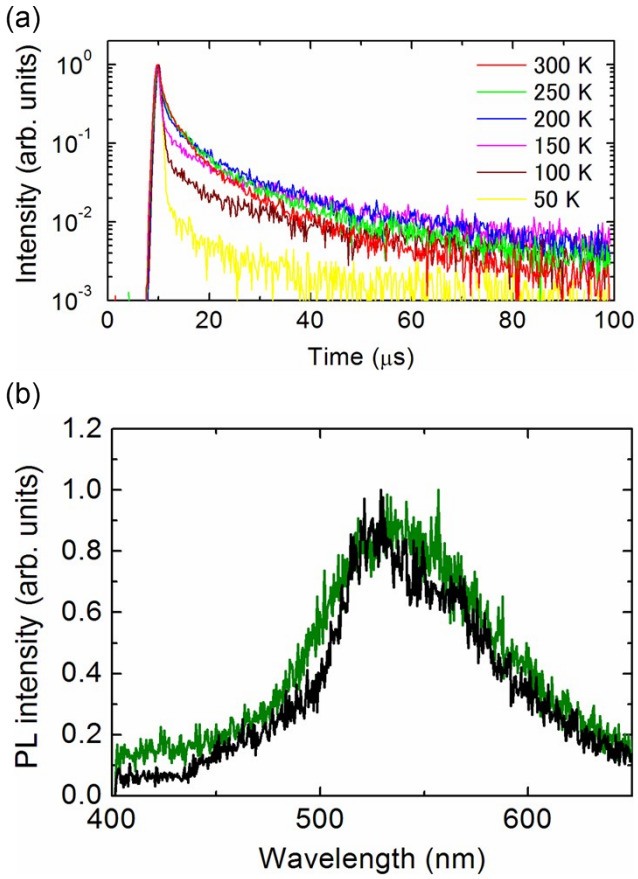
Compound	λ_{ab} (nm)		λ_{em} (nm)	
	Calc.	Exp.	Calc.	Exp.
DHPZ-2BI	421	428	566	550
DHPZ-2BN	473	420	562	545
DHPZ-2BTZ	495	450	609	605
DHPZ-2TRZ	513	479	627	648

8. Calculated S_1-T_1 energy gaps

Supplementary Table S3: S_1-T_1 energy gaps (ΔE_{ST}) of DHPZ-2BI, DHPZ-2BN, DHPZ-2BTZ, and DHPZ-2TRZ calculated using the TD-CAM-B3LYP/cc-pVDZ//CAM-B3LYP/cc-pVDZ method.

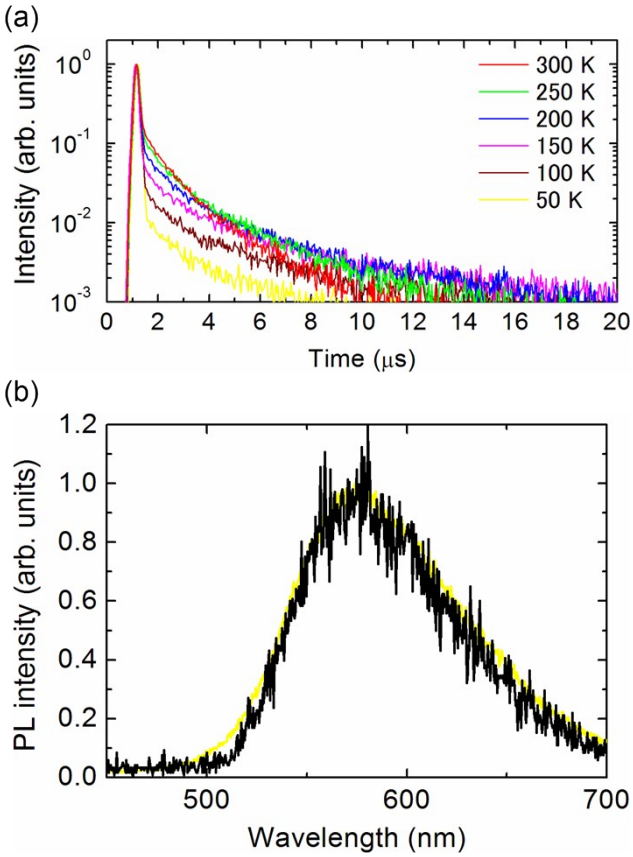
Compound	ΔE_{ST} (eV)
DHPZ-2BI	0.83
DHPZ-2BN	0.60
DHPZ-2BTZ	0.52
DHPZ-2TRZ	0.42

9. Photoluminescence characteristics of a 6 wt% DHPZ-2BN:*m*-CBP film.



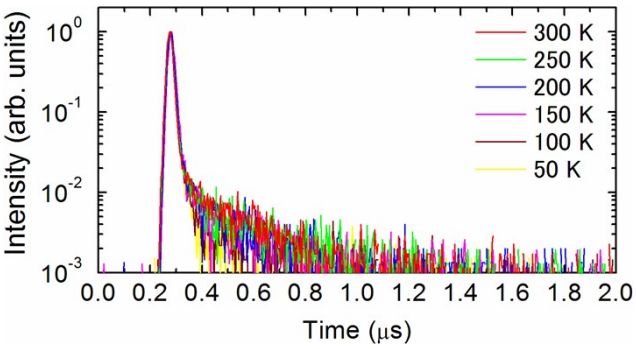
Supplementary Fig. S1: (a) Transient PL decay curves for a 6 wt% DHPZ-2BN:*m*-CBP film measured at temperatures of 50 to 300 K. (b) Fluorescence and phosphorescence spectra of the doped film measured at 4 K. Green and black lines show fluorescence and phosphorescence spectra, respectively.

10. Photoluminescence characteristics of a 6 wt% DHPZ-2BTZ:*m*-CBP film.



Supplementary Fig. S2: (a) Transient PL decay curves for a 6 wt% DHPZ-2BTZ:*m*-CBP film measured at temperatures of 50 to 300 K. (b) Fluorescence and phosphorescence spectra of the doped film measured at 4 K. Yellow and black lines show fluorescence and phosphorescence spectra, respectively.

11. Transient photoluminescence decays for a 6 wt% DHPZ-2TRZ:*m*-CBP film.



Supplementary Fig. S3: Transient PL decay curves for a 6 wt% DHPZ-2TRZ:*m*-CBP film measured at temperatures of 50 to 300 K.

References

S1. X.-Q. Zhu, Z. Dai, A. Yu, S. Wu, J.-P. Cheng, *J. Phys. Chem. B*, **112**, 11694-11707 (2008).

S2. M. Debeaux, M. W. Thesen, D. Schneidenbach, H. Hopf, S. Janietz, H. Krüger, A. Wedel, W. Kowalsky, H.-H. Johannes, *Adv. Funct. Mater.*, **20**, 399-408 (2010).

S3. H. Tanaka, K. Shizu, H. Miyazaki, C. Adachi, *Chem. Commun.* **48**, 11392-11394 (2012).