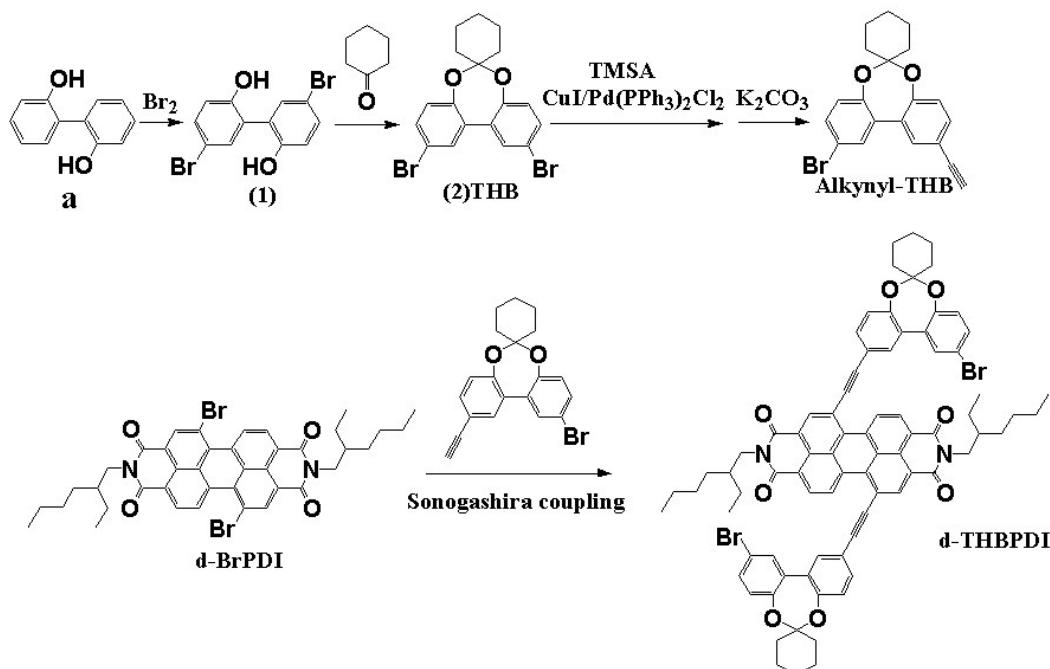


# Base-Driven Keto-Enol Anion Tautomerism of Perylene Diimide Derivative in DMF Solution

Jianmin Wang, Enfang He, Hailong Wang, Wenlong Hou, Jing Xu, Xiao Wang, Huiyun Guo,  
Zhenlin Zhang, Ruijun Zhang,\* Haiquan Zhang\*

State Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao 066004, PR  
China

\*Corresponding author. E-mail: zhangrj@ysu.edu.cn; hqzhang@ysu.edu.cn



Scheme 1 synthesis route of d-THBPDI

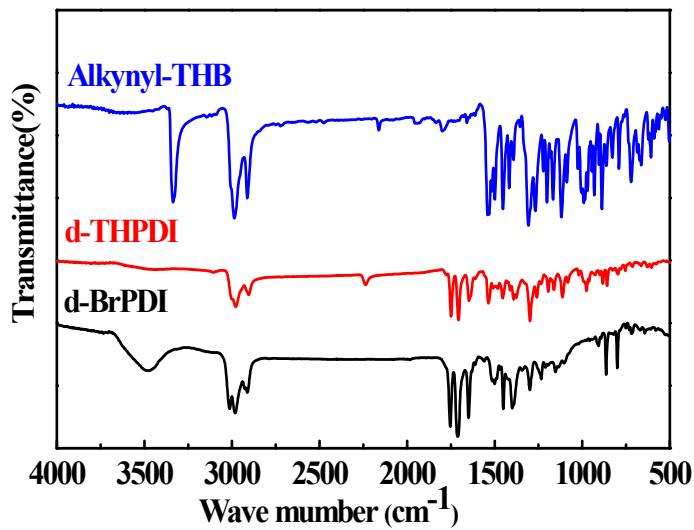


Fig. S1 FT-IR spectra of d-BrPDI, Alkynyl-THB and title compound d-THBPD

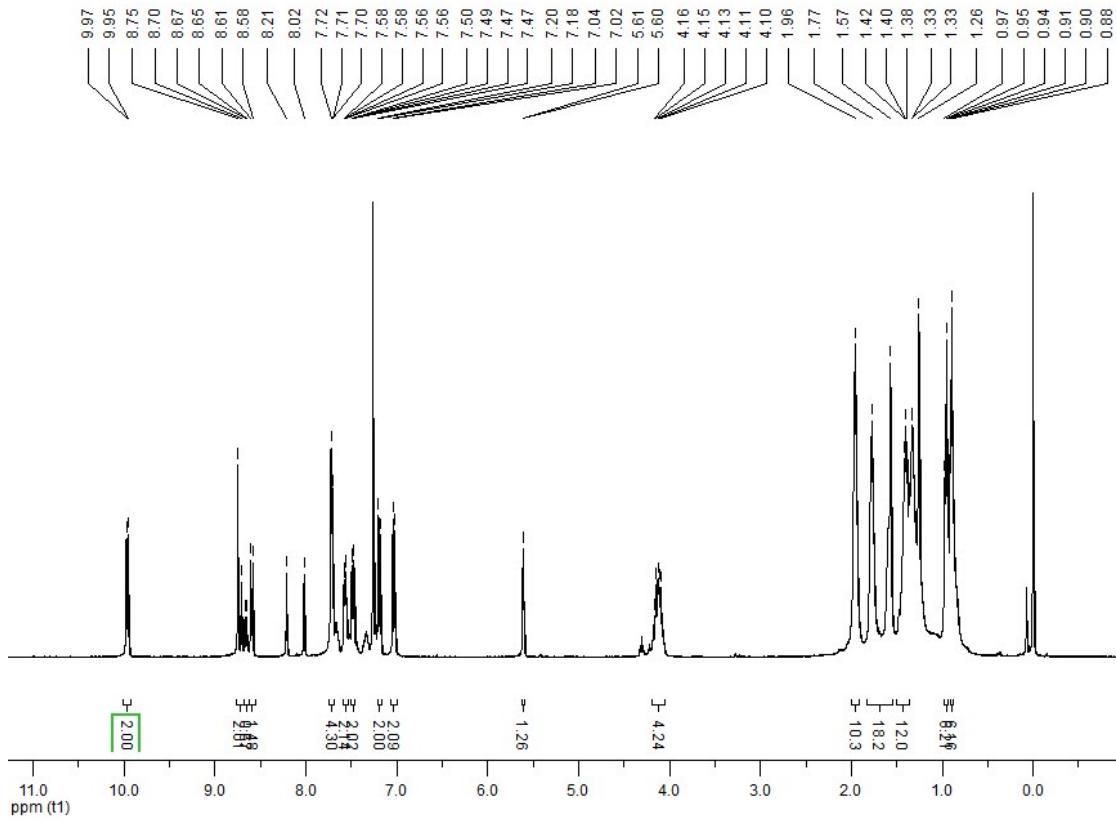


Fig. S2  $^1\text{H}$  NMR spectra of title compound d-THBPD

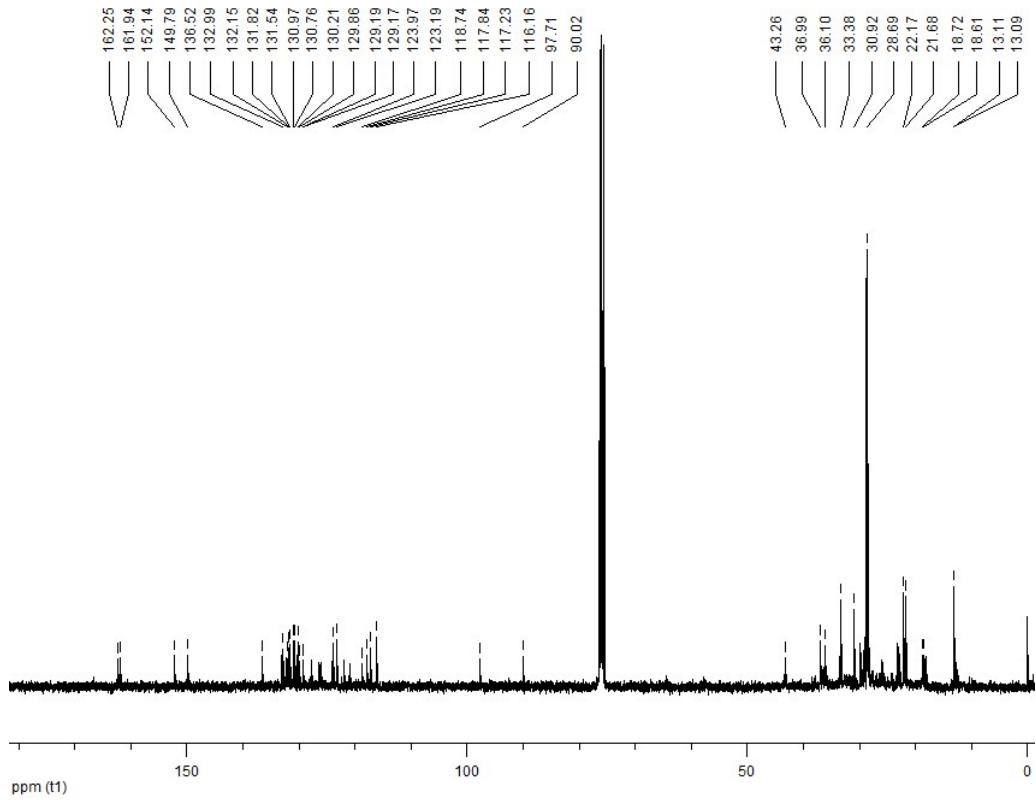


Fig. S3 <sup>13</sup>C NMR spectra of title compound d-THBPDI

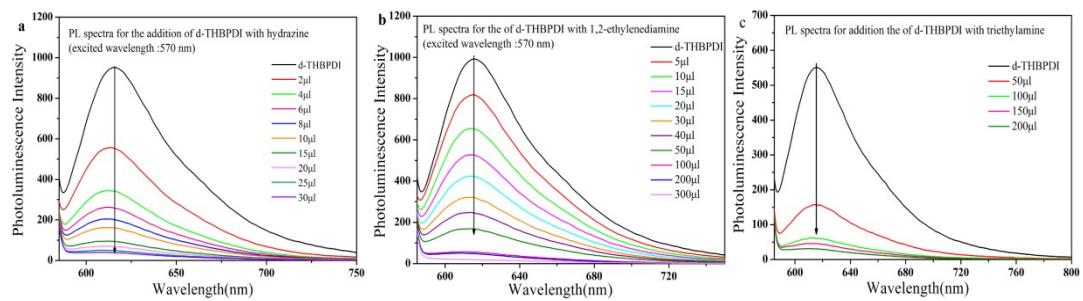
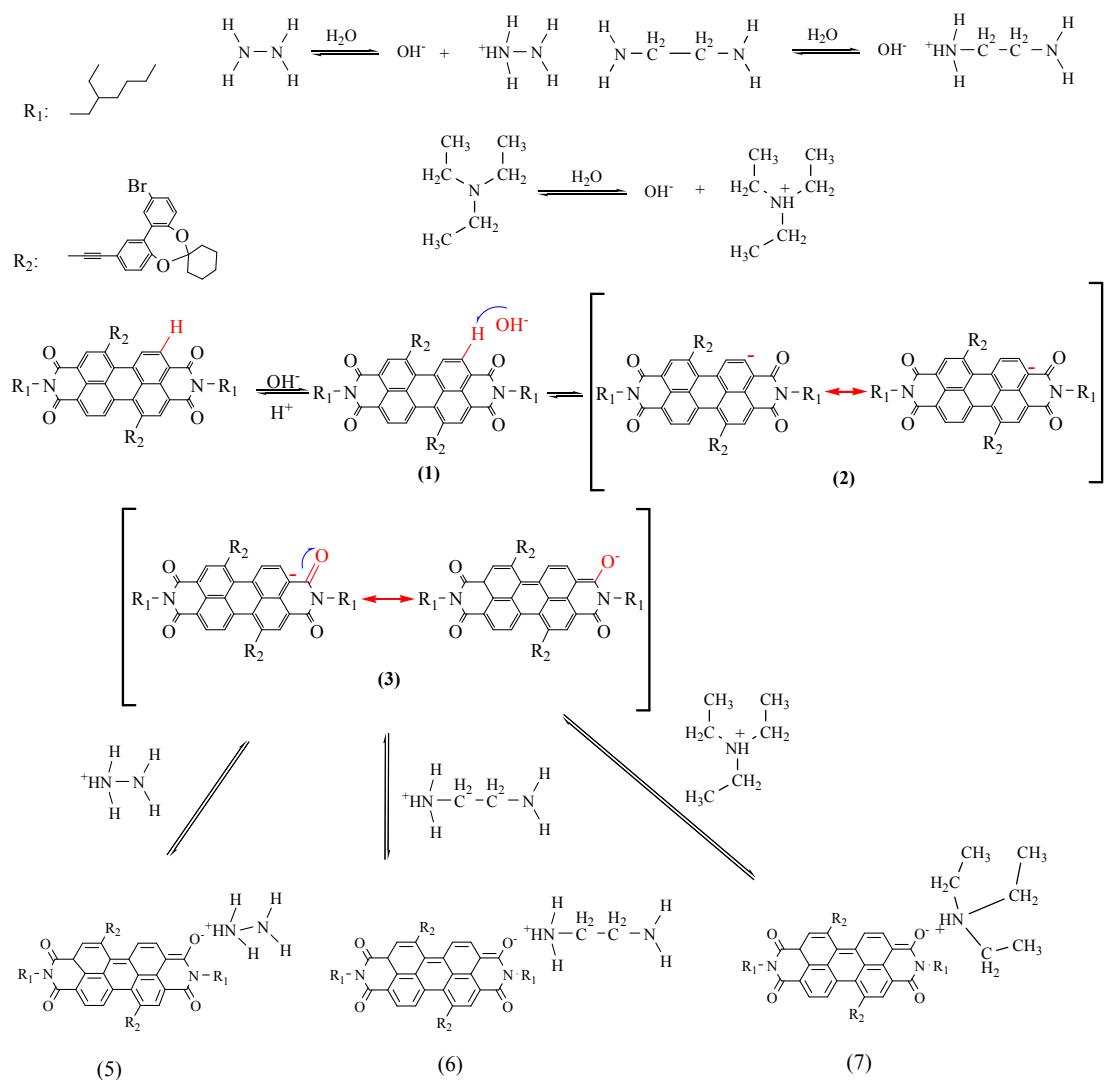
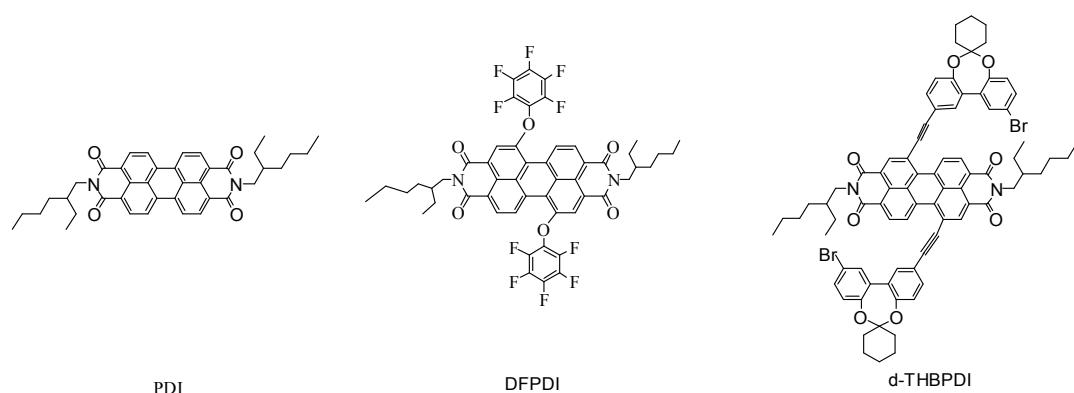


Fig. S4 Photoluminescence spectra of d-THBPDI upon adding various organic bases of different volume



Scheme 2 Organic base-driven keto-enol anion tautomerism mechanism of  $\text{d-THBPDI} \leftrightarrow \text{d-THBPDI}^-$



Scheme 3 The molecule structure of PDI, DFPDI and d-THBPDI.

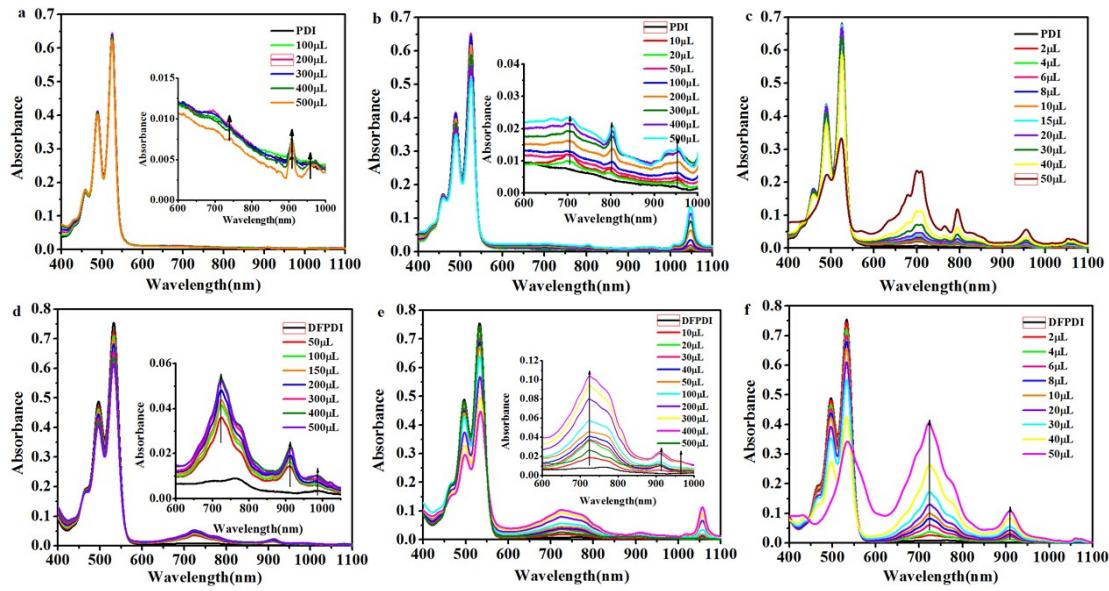


Fig. S5 UV-vis spectra of PDI (a, b and c) and DFPDI (d, e and f) in the different amount of triethylamine, ethanediamine and hydrazine, respectively.

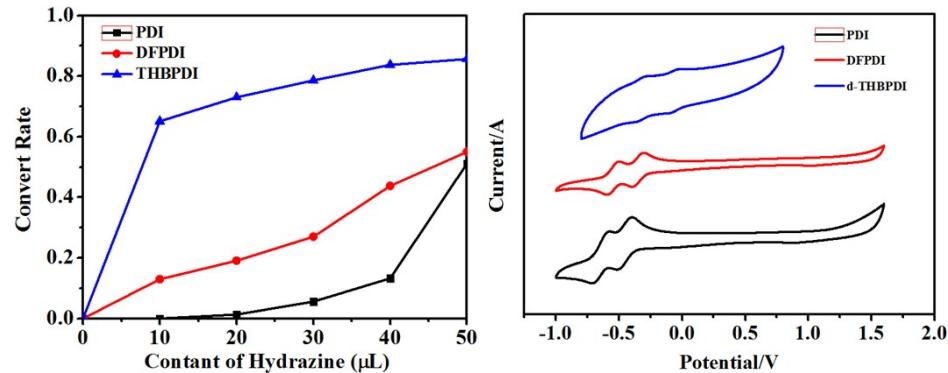


Fig. S6 The convert rate of PDI, DFPDI and d-THBPDI with addition of hydrazine (a) Cyclic voltammetry of PDI, DFPDI and d-THBPDI containing  $[\text{nBu}_4\text{N}][\text{PF}_6]$  (0.1M) with respect to  $\text{Ag}/\text{AgCl}$  in DMF (b)

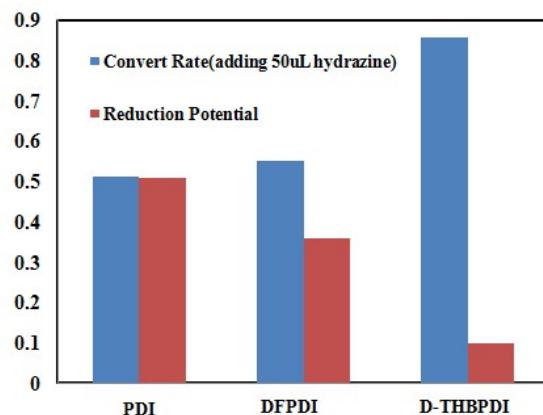


Fig. S7 The convert rate of PDI, DFPDI and d-THBPDI with adding 50 $\mu\text{L}$  hydrazine (blue) and their absolute value of reduction potential (red).