

## Supporting Information

### **High-contrast mechanochromic fluorescence from a highly solid-state emissive 2-(dimesitylboryl)phenyl-substituted [2.2]paracyclophane**

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## General Methods

Fluorescence spectra measurements were performed with a Hitachi F-7000 spectrometer. The X-ray diffraction (XRD) analysis was performed on a Rigaku Dmax X-ray diffractometer (45 kV, 200 mA) with Cu-K $\alpha$  radiation at room temperature and  $2\theta$  between 5° to 90°.

## Photophysical Properties

**Table S1.** Emission data of *g*-BPhNMe<sub>2</sub>-Cp.

	$\lambda_{em}/nm$	$\Phi_F$
cyclohexane	488	0.83 <sup>a</sup>
pristine powder	439	0.58 <sup>b</sup>
ground powder	496	0.73 <sup>b</sup>

<sup>a</sup> Calculated using fluorescein as a standard in degassed solutions. <sup>b</sup> Absolute quantum yields were determined using an integrating sphere.

## Theoretical Calculations

All the calculations were conducted using the Gaussian 09, revision B01,<sup>1</sup> software package and the density functional (DFT) and basis set PBE0/6-31G(d) were used. The S<sub>0</sub>-geometries were optimized by the DFT method using the X-ray crystal structure as the initial geometry. Based on the optimized S<sub>0</sub>-geometries, the optimizations of S<sub>1</sub>-geometries and the transition properties of the S<sub>1</sub> were calculated by the time-dependent DFT (TD-DFT) method. To ensure the optimized geometry being a local minimum, the frequencies of all geometry optimizations were calculated and there are not any imaginary frequencies. The geometry optimizations for the crystalline phase were performed on the central molecule while the adjacent molecules were fixed in the initial geometries.

**Table S1.** Calculated transition properties of *g*-BPhNMe<sub>2</sub>-Cp.

morphological phase	transition	composition	$E/eV$	$\lambda/nm$	$f$
crystalline phase	S <sub>0</sub> →S <sub>1</sub>	H→L (71)	3.37	368	0.048
		H-1→L (28)			
amorphous phase	S <sub>1</sub> →S <sub>0</sub>	H→L (99)	2.53	489	0.0336
	S <sub>0</sub> →S <sub>1</sub>	H→L (87)	3.31	374	0.0541
		H-1→L (9)			
	S <sub>1</sub> →S <sub>0</sub>	H→L (99)	2.24	552	0.0357

## References

(1) Gaussian 09, Revision B.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; 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, J. A., Jr.; 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, Inc., Wallingford CT, **2010**.