Electronic Supplementary Material (ESI) for New Journal of Chemistry.

SUPPORTING INFORMATION

Turn-on fluorescent sensor for the detection of lipopolysaccharide based on a novel bispyrenyl terephtalaldehyde-bis-guanylhydrazone

Kriangsak Khownium,[*a] Jariya Romsaiyud,[b] Suparerk Borwornpinyo,[c,d] Preedajit Wongkrasant,[e] Pawin Pongkorpsakol,[e] Chatchai Muanprasat,[e,d] Bundet Boekfa,[f] Tirayut Vilaivan,[g] Somsak Ruchirawat,[h] and Jumras Limtrakul[i]

[a]Faculty of Medicine, King Mongkut's Institute of Technology Ladkrabang, Bangkok, 10520, Thailand
[b]Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Ramkhamhaeng University, Huamark, Bangkapi, Bangkok 10240, Thailand
[c]Department of Biotechnology and [d]Excellent Center for Drug Discovery, and [e]Department of Physiology Faculty of Science, Mahidol University, Bangkok 10400, Thailand
[f]Chemistry Department, Faculty of Liberal Arts and Science, Kasetsart University Kamphaeng Saen Campus, Nakhon Pathom 73140, Thailand
[g]Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand
[h]Chulabhorn Research Institute, Vipavadee-Rangsit Highway, Bangkok 10210, Thailand
[i]Department of Materials Science and Engineering, School of Molecular Science and Engineering, Vidyasirimedhi Institute of Science and Technology, Rayong 21210, Thailand

*Correspondence to Kriangsak Khownium, kriangsak.kh@kmitl.ac.th

Table of Contents **Page**

1. Spectroscopic data of synthesized compounds S2

2. Absorption spectra of **BPTG** before and after the addition of LPS S10

3. The photophysical properties of **BPTG** S10

4. Results of computational experiments S11

1. Spectroscopic data of synthesized compounds

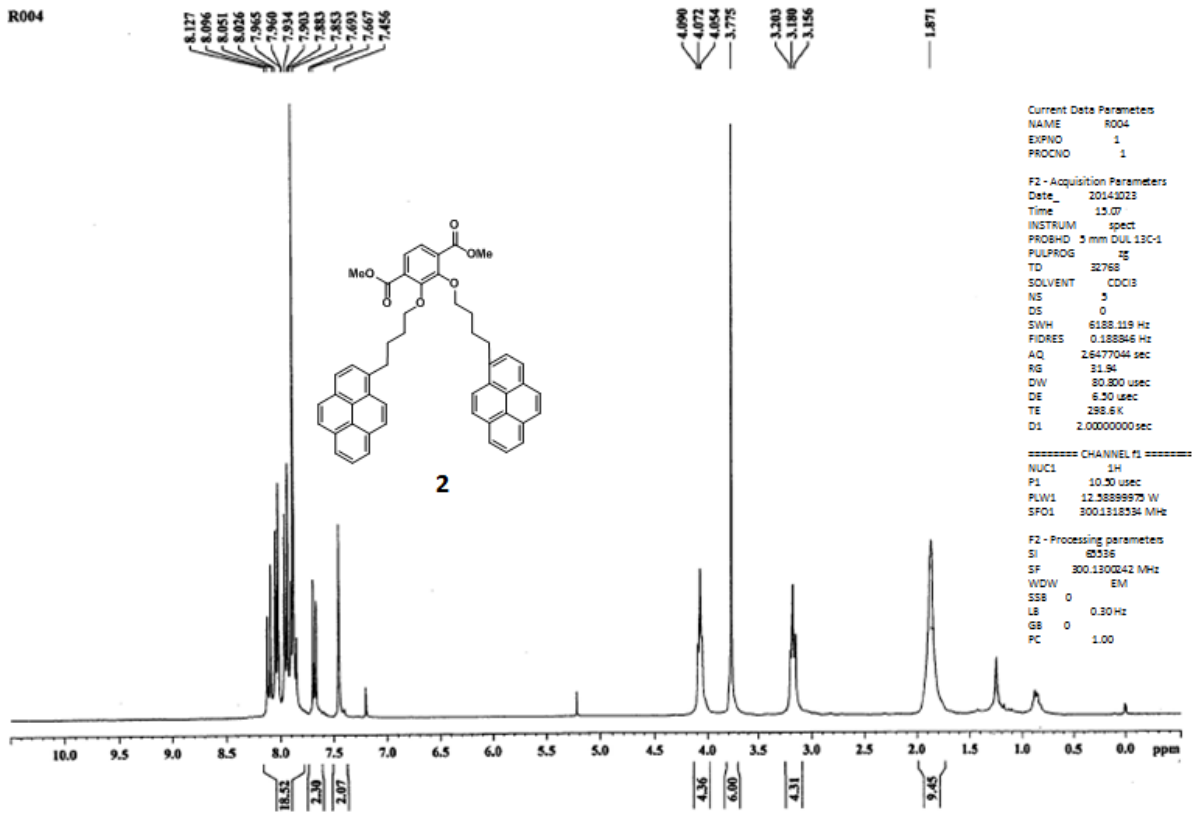


Fig. S1 ^{1}H NMR spectrum of dimethyl 2,3-bis(4-(pyren-1-yl)butoxy)terephthalate (**2**)

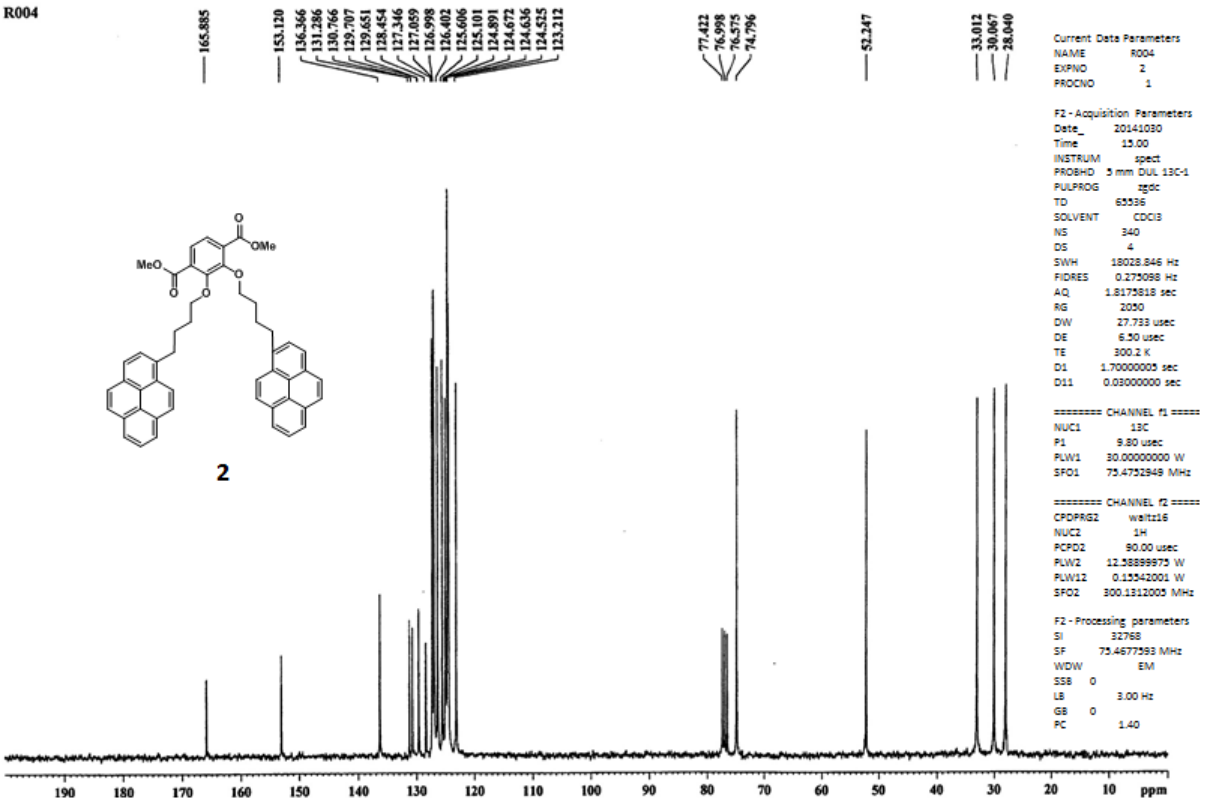


Fig. S2 ^{13}C NMR spectrum of dimethyl 2,3-bis(4-(pyren-1-yl)butoxy)terephthalate (**2**)

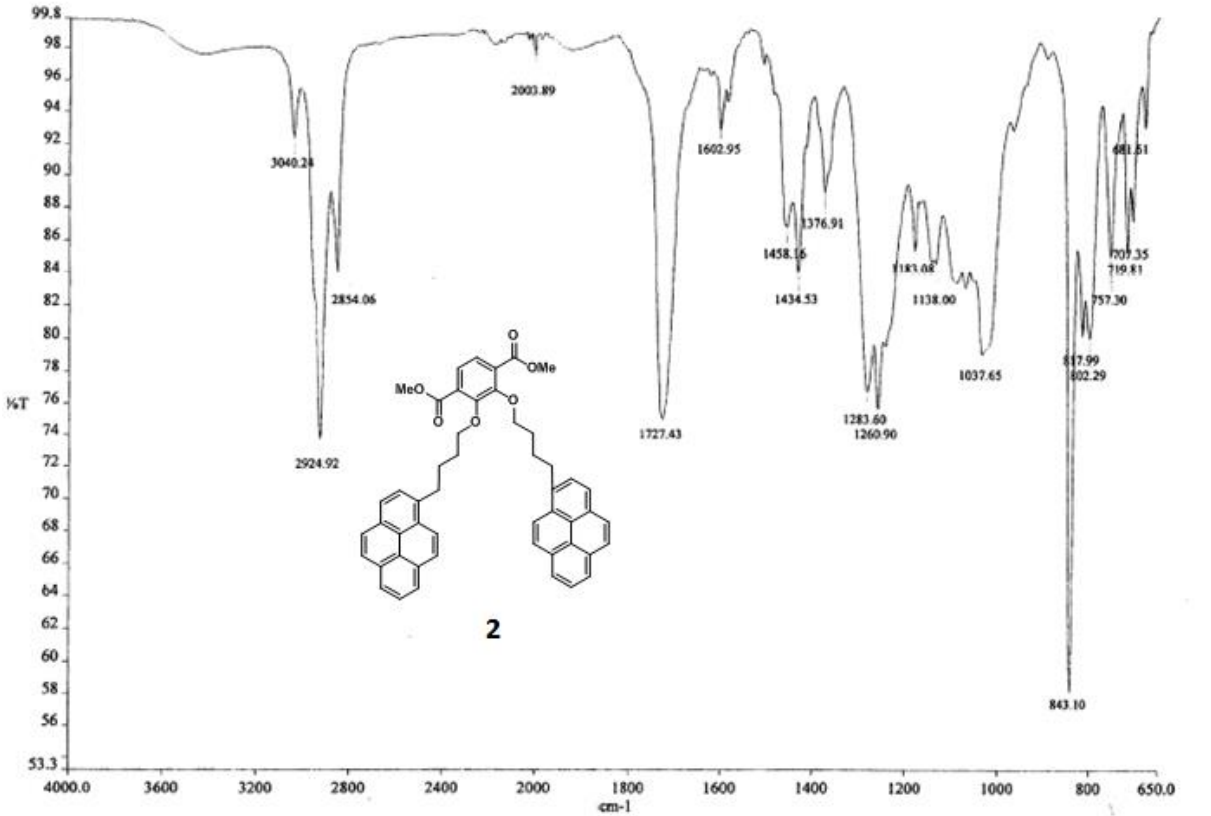


Fig. S3 IR spectra of dimethyl 2,3-bis(4-(pyren-1-yl)butoxy)terephthalate (**2**)

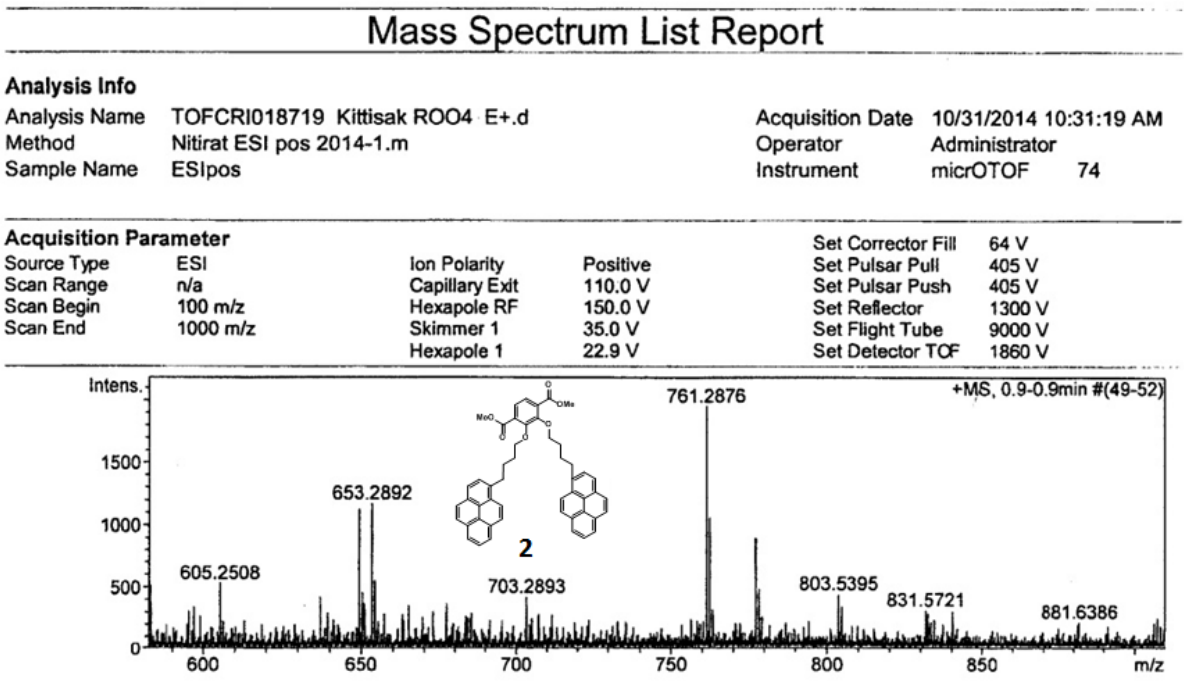


Fig. S4 ESI-MS of dimethyl 2,3-bis(4-(pyren-1-yl)butoxy)terephthalate (**2**)

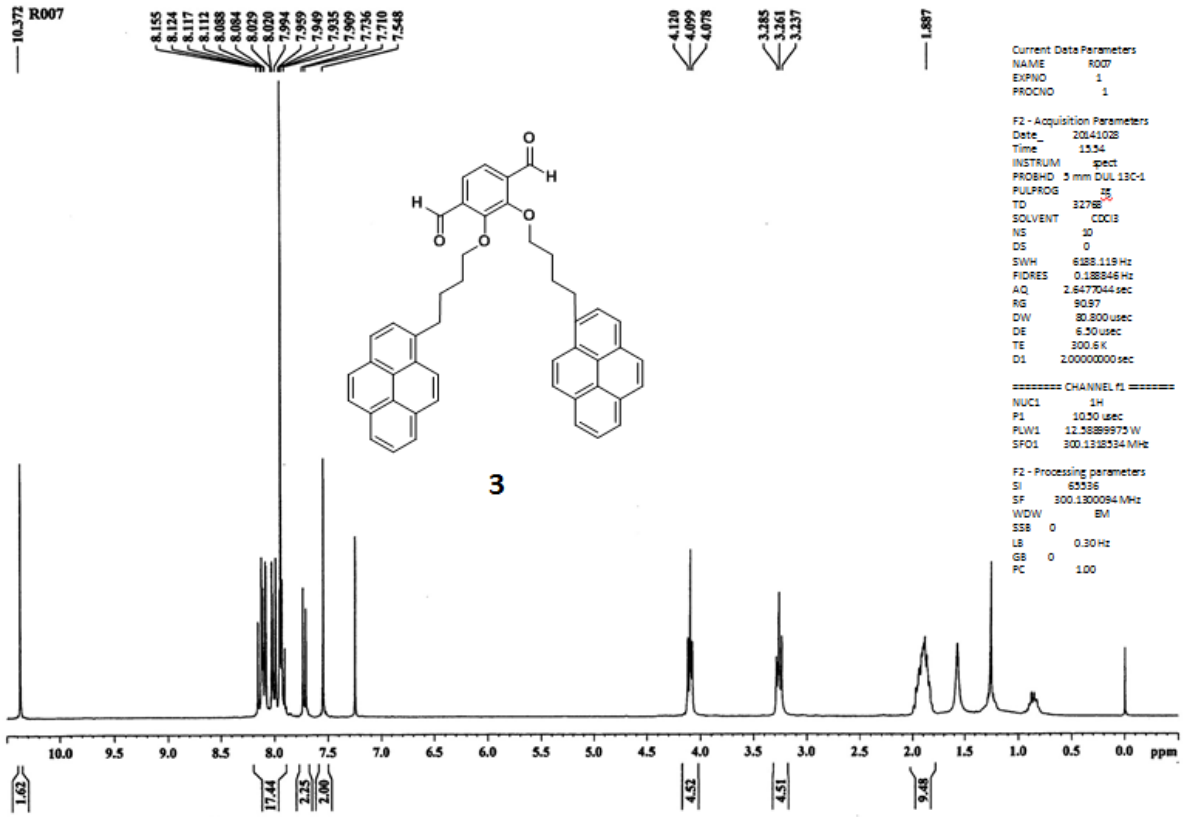


Fig. S5 ^{1}H NMR spectrum of 2,3-bis(4-(pyren-1-yl)butoxy)terephthalaldehyde (**3**)

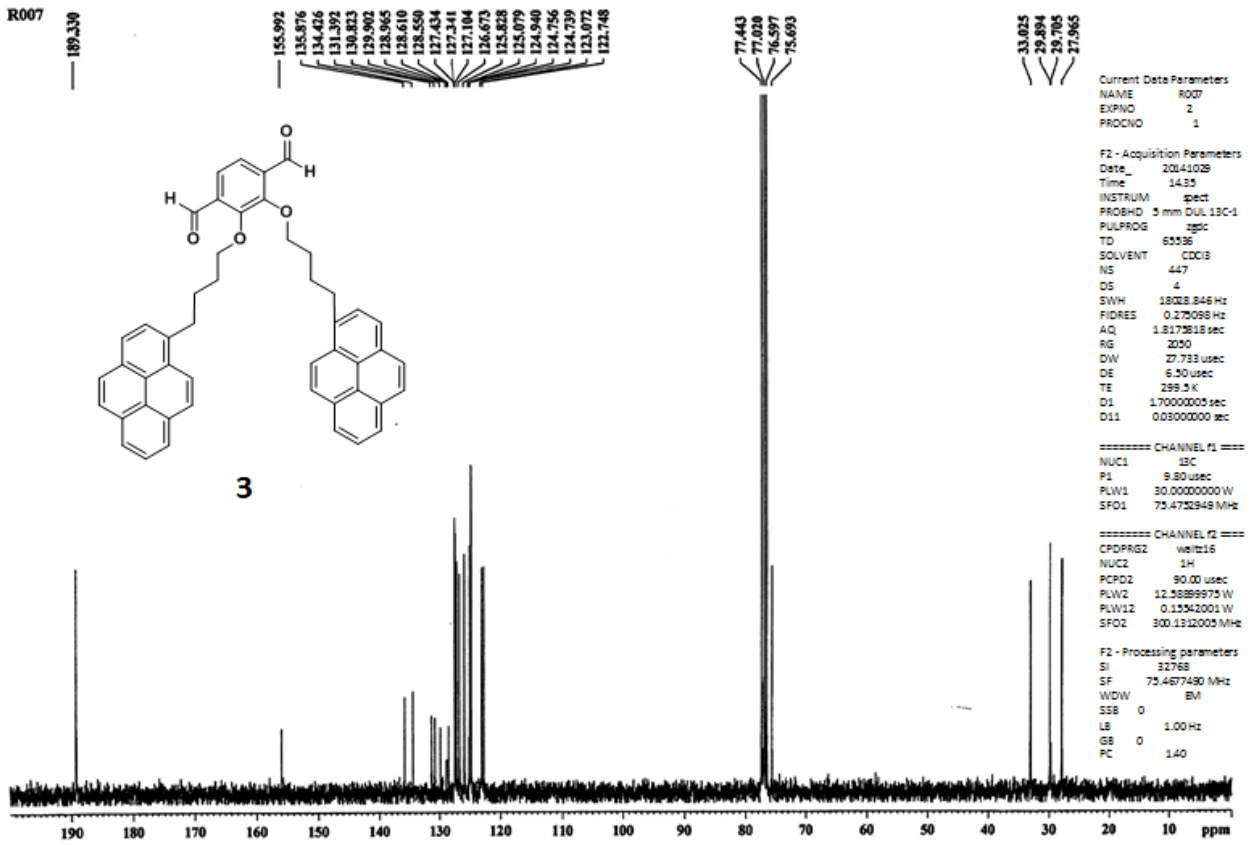


Fig. S6 ^{13}C NMR spectrum of 2,3-bis(4-(pyren-1-yl)butoxy)terephthalaldehyde (**3**)

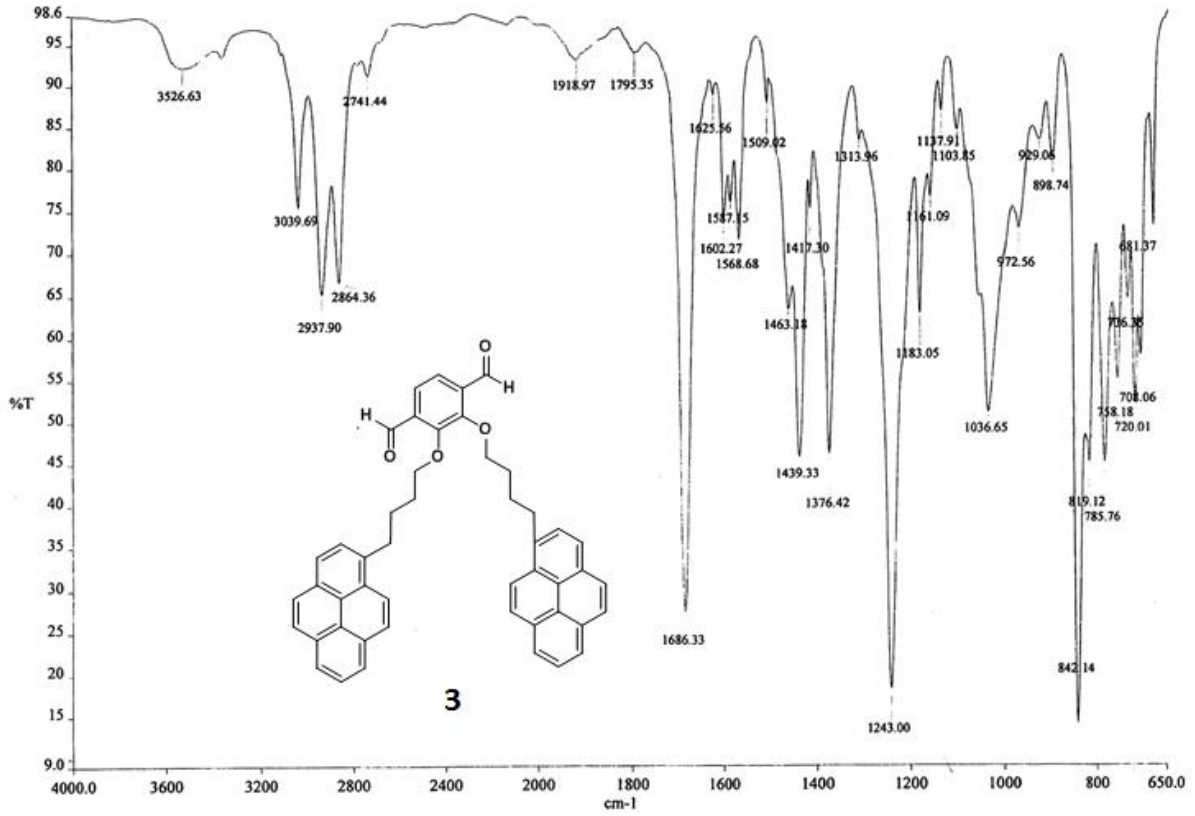


Fig. S7 IR spectra of 2,3-bis(4-(pyren-1-yl)butoxy)terephthalaldehyde (**3**)

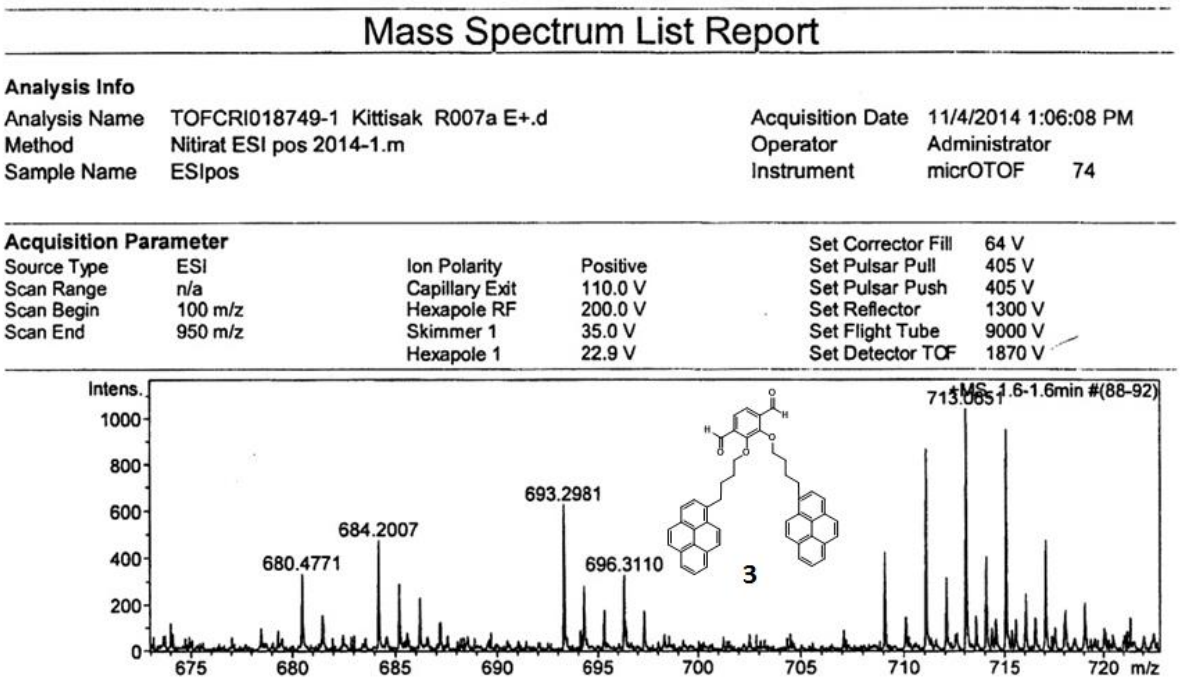


Fig. S8 ESI-MS of 2,3-bis(4-(pyren-1-yl)butoxy)terephthalaldehyde (**3**)

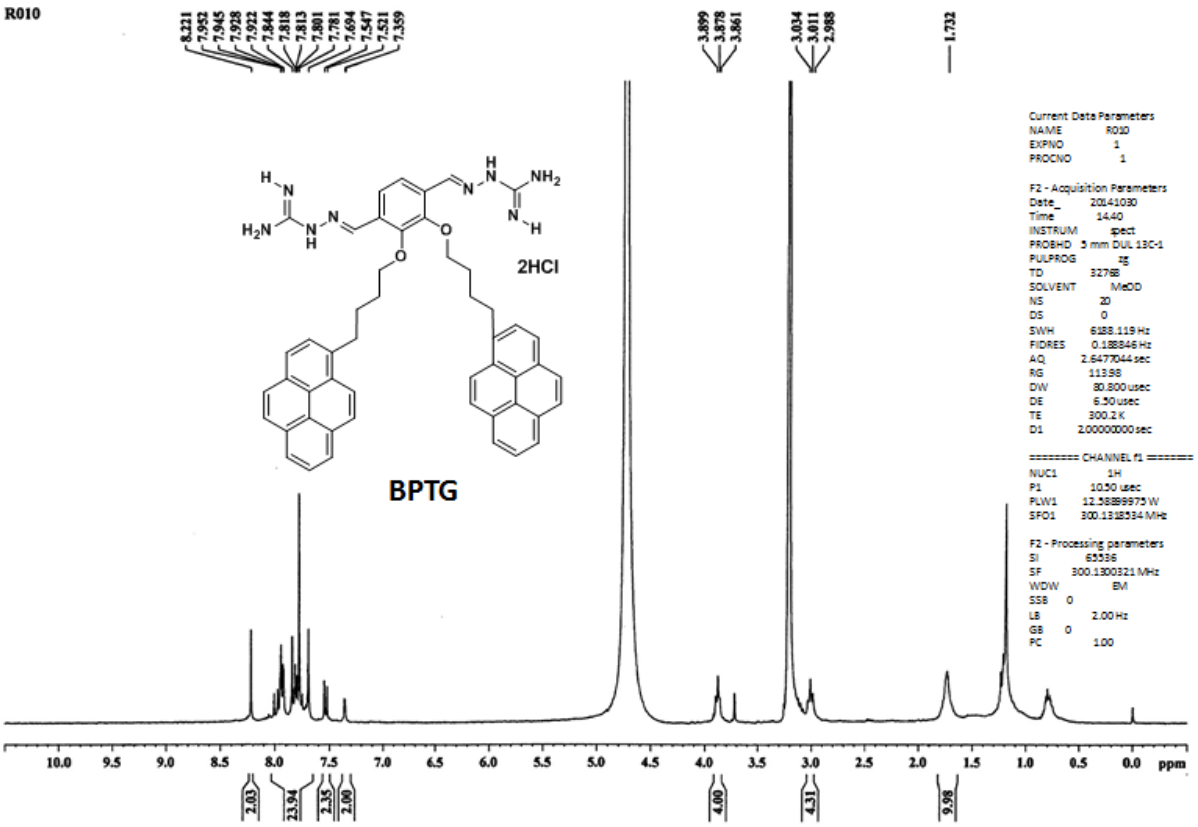


Fig. S9 ^{1}H NMR spectrum of 2E,2'E)-2,2'-((2,3-bis(4-(pyren-1-yl)butoxy)-1,4-phenylene)bis(methanylylidene))bis(hydrazinecarboximidamide) (**BPTG**)

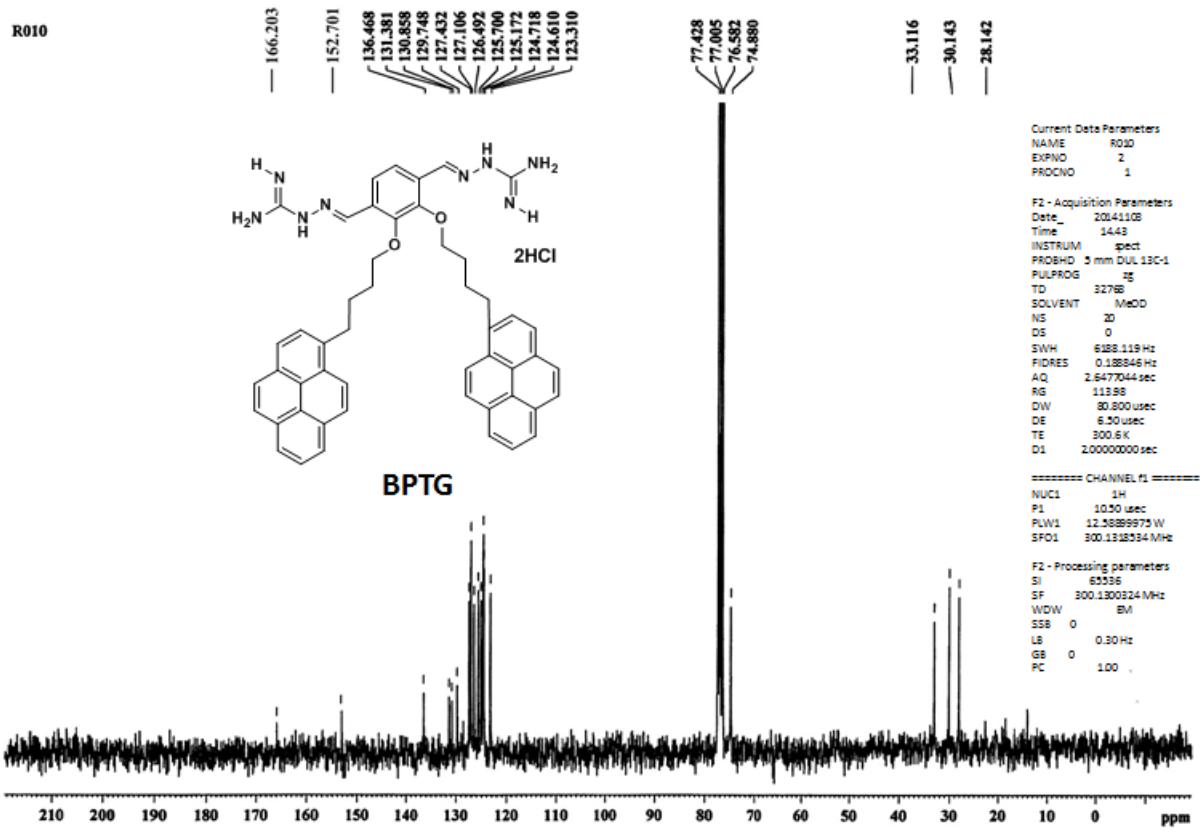


Fig. S10 ^{13}C NMR spectrum of 2E,2'E)-2,2'-((2,3-bis(4-(pyren-1-yl)butoxy)-1,4-phenylene)bis(methanylylidene))bis(hydrazinecarboximidamide) (**BPTG**)

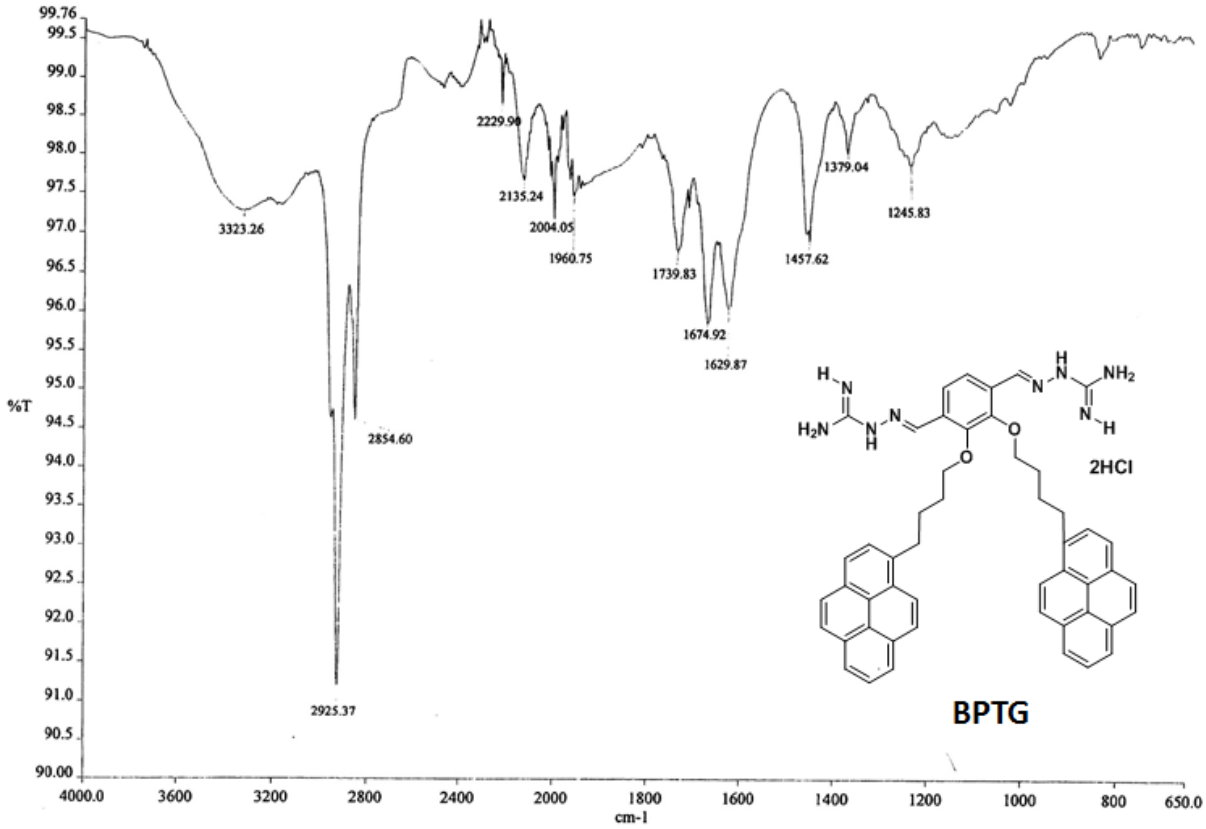


Fig. S11 IR spectra of 2E,2'E)-2,2'-((2,3-bis(4-(pyren-1-yl)butoxy)-1,4-phenylene)bis(methanylylidene))bis(hydrazinecarboximidamide) (**BPTG**)

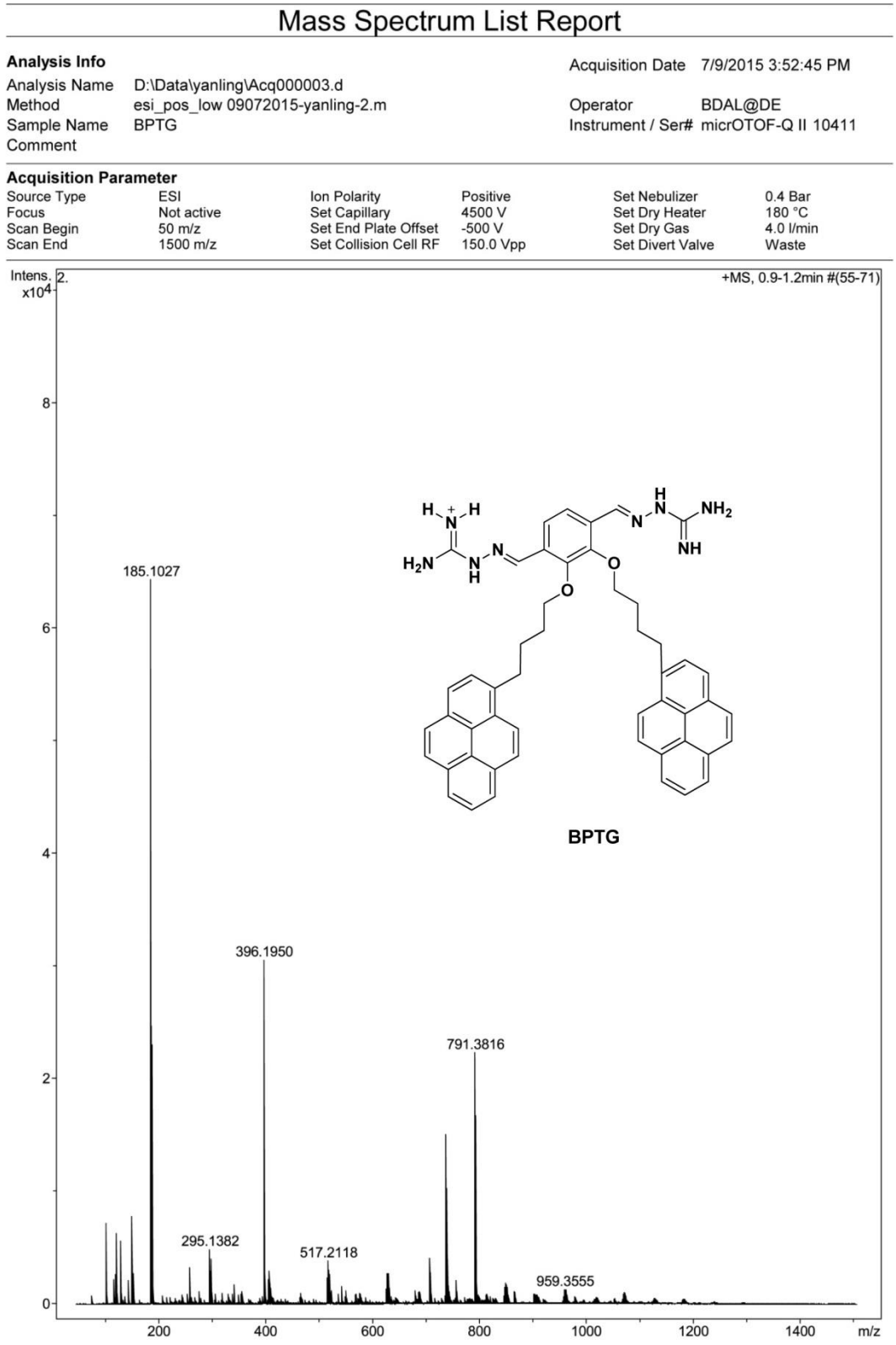


Fig. S12 ESI-MS of 22E,2'E)-2,2'-((2,3-bis(4-(pyren-1-yl)butoxy)-1,4-phenylene)bis(methanylylidene))bis(hydrazinecarboximidamide) (**BPTG**)

2. Absorption spectra of BPTG before and after the addition of LPS

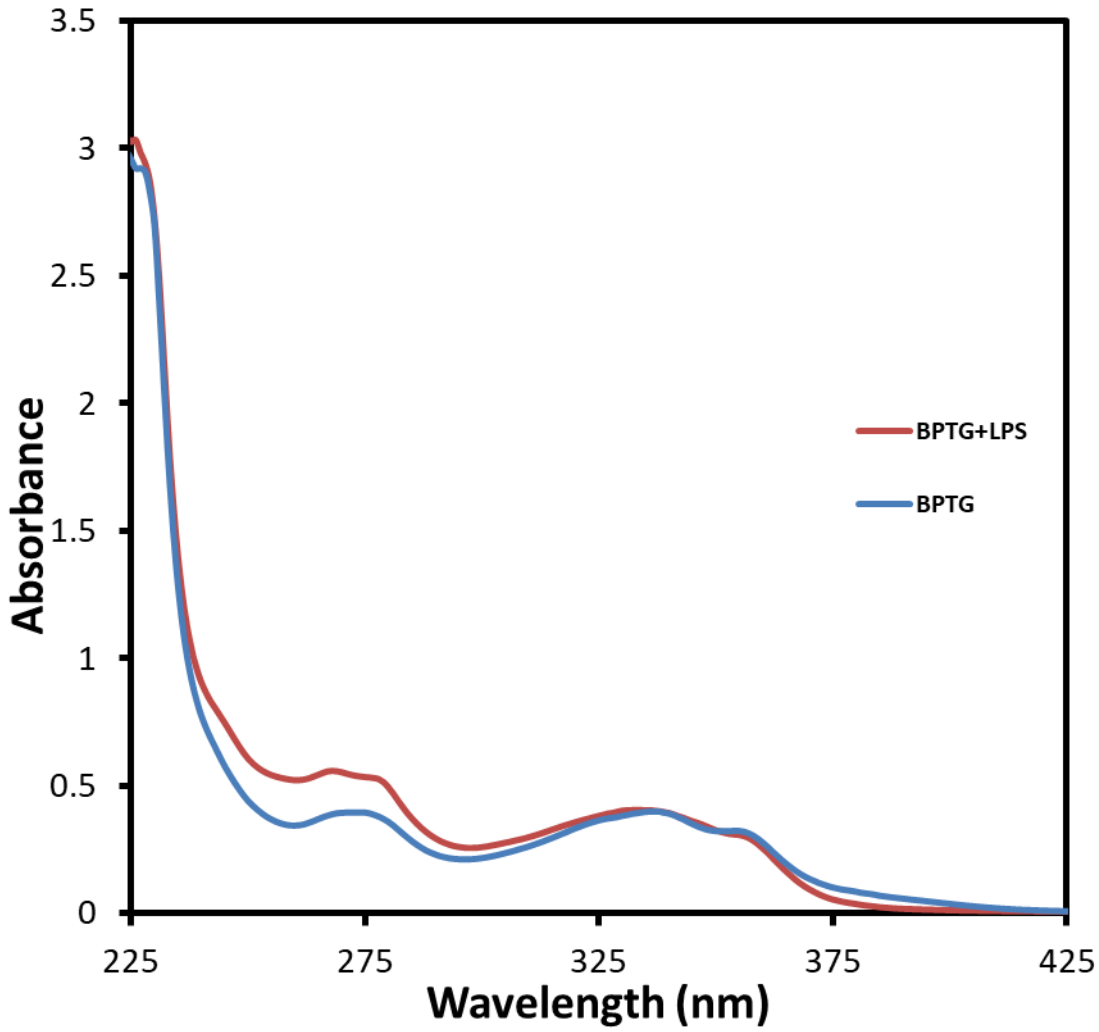


Fig. S13 Absorption spectra of **BPTG** (5 μM) in a solution of DMSO/HEPES (v/v = 1/6) buffer (10 mM, pH 7.4) before and after addition of LPS (10 μM). The UV-vis absorbance maximum at 342 nm is corresponding to the pyrenyl band.

3. The photophysical properties of BPTG

Table S1. Photophysical properties of BPTG in a solution of DMSO/HEPES (v/v = 1/6) buffer (10 mM, pH 7.4) before and after addition of LPS.

Compound	Absorption		Emission	
	λ_{max}(nm)	ε ($M^{-1}cm^{-1}$)	λ_{em}(nm)	Φ_F[a]
BPTG	**342**	**76,320**	**485**	**0.072**
BPTG + LPS	**342**	**78,537**	**485**	**0.090**

a : Quinine sulfate in 0.1 M H_2SO_4 (Φ_F = 0.54) was used as standard

4. Results of computational experiments

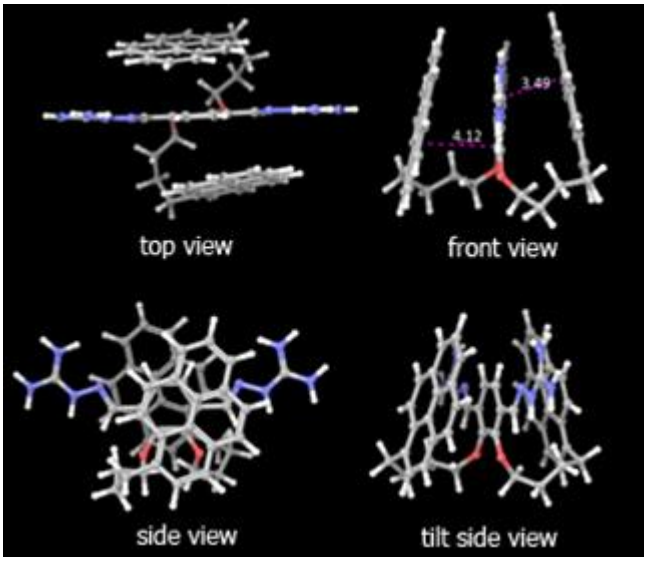
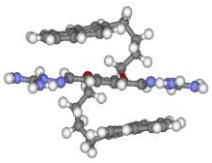
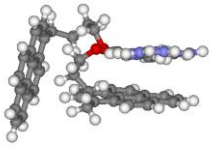
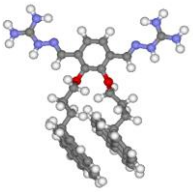


Fig. S14 Sandwich stacking conformation of **BPTG** like a butterfly-like skeleton

Table S2. BPTG's conformations and their total energies, HOMO's enegies, LUMO's enegies and band gap of (a) sandwich- (b) semi- and (c) open-stacking optimized with the M06-2X functional in Gaussian 09 program.

BPTG's Conformation			
	sandwish-	**semi-**	**open-**
Total Energy (au)	-2521.337149	-2521.330214	-2521.312463
Relative Energy (kcal/mol)	**0.00**	**4.35**	**15.49**
LUMO (au)	-0.21554	-0.22098	-0.23608
HOMO (au)	-0.38725	-0.36041	-0.32508
band gap (eV)	4.67257252	3.79416916	2.421868

The M06 functional was developed by Zhao and Truhlar. [1-3] The M06 functional, which take care the van der Waals interaction, has been successful studied on the adsorption and reaction on several material such as zeolite,[4] alloy metal,[5] porphyrin[6] and metal-organic framework.[7] We optimized all structures with Gaussian 09 program.[8]

References

(1) Zhao, Y.; Schultz, N. E.; Truhlar, D. G. "Design of density functionals by combining the method of constraint satisfaction with parametrization for thermochemistry, thermochemical kinetics, and noncovalent interactions" *J. Chem. Theory Comput.* **2006**, *2*, 364-82.

(2) Zhao, Y.; Truhlar, D. G. "The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: Two new functionals and systematic testing of four M06-class functionals and 12 other functionals" *Theor. Chem. Acc.* **2008**, *120*, 215-41.

(3) Zhao, Y.; Truhlar, D. G. "Benchmark data for interactions in zeolite model complexes and their use for assessment and validation of electronic structure Methods" *J. Phys. Chem. C* **2008**, *112*, 6860-8.

(4) Boekfa, B.; Choomwattana, S.; Khongpracha, P.; Limtrakul, J. "Effects of the Zeolite Framework on the Adsorptions and Hydrogen-Exchange Reactions of Unsaturated Aliphatic, Aromatic, and Heterocyclic Compounds in ZSM-5 Zeolite: A Combination of Perturbation Theory (MP2) and a Newly Developed Density Functional Theory (M06-2X) in ONIOM Scheme" *Langmuir* **2009**, *25*, 12990-9.

(5) Boekfa, B.; Pahl, E.; Gaston, N.; Sakurai, H.; Limtrakul, J.; Ehara, M. "C-Cl Bond Activation on Au/Pd Bimetallic Nanocatalysts Studied by Density Functional Theory and Genetic Algorithm Calculations" *J. Phys. Chem. C* **2014**, *118*, 22188-96.

(6) Maitarad, P.; Namuangruk, S.; Zhang, D.; Shi, L.; Li, H.; Huang, L.; Boekfa, B.; Ehara, M. "Metal-Porphyrin: A Potential Catalyst for Direct Decomposition of N2O by Theoretical Reaction Mechanism Investigation" *Environ. Sci. Technol.* **2014**, *48*, 7101-10.

(7) Maihom, T.; Choomwattana, S.; Khongpracha, P.; Probst, M.; Limtrakul, J. "Formaldehyde encapsulated in lithium-decorated metal-organic frameworks: A density functional theory study" *ChemPhysChem* **2012**, *13*, 245-9.

(8) 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.; Sonnen 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.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; 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, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09, Gaussian, Inc., Wallingford CT.* **2009**.