Dibenzo[f,h]furo[2,3-b]quinoxaline-based molecule scaffold as deep blue fluorescence materials for organic light-emitting diodes

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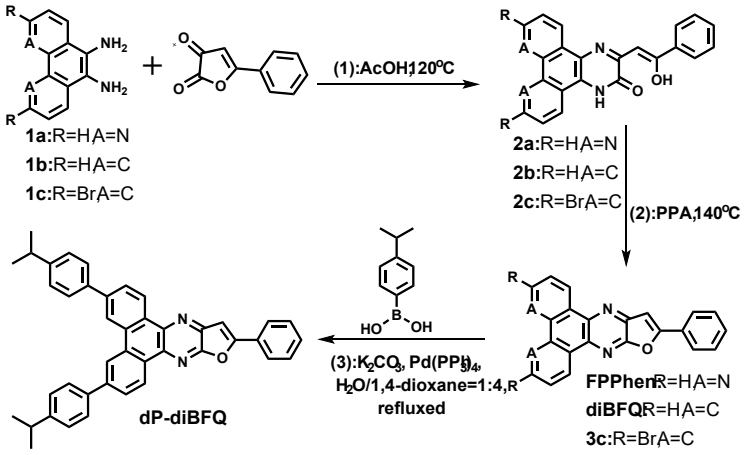
Electronic Supplementary Information

Contents

Section 1:Computational details

Molecular geometry optimizations for the ground (S0) states were performed at the PBE0/6-31G(d) level and the vertical excitation energies for 40 singlet states were estimated with time-dependent density function theory (TD-DFT) at the B3LYP/6-31G(d) level. The first singlet excited states (S1) for all relevant structures were optimized by TD-PBE0/6-31G(d) level and the emission energies were also evaluated by TD-PBE0/6-311G(d,p). All computations were conducted by using Gaussian 09 program.[2-5]

Section 2:



Scheme S1 the synthesis route of diBFQ, FPPhen, dP-diBFQ.

All reagents were used without further purification. The ^{1}HNMR spectra were recorded on Bruker Avance 400MHz spectrometers and HRMS experiments were carried out on a Thermo Scientific LTQ Orbitrap Discovery (Bremen, Germany).

General procedure for synthesizing diBFQ, FPPhen and 3c

A 250 mL 3-neck flask was added the phenanthrene-9,10-diamine/3,6-dibromophenanthrene-9,10-diamine/ 1,10-phenanthroline-5,6-diamine (3.8 mmol), 5-phenylfuran-2,3-dione (0.66 g, 3.8 mmol) and acetate acid (50 mL). The mixture was heated to 110 °C for 8 h under nitrogen. After the reaction was finished, the reaction mixture allowed to cool down to room temperature and poured into water. The solid was collected by filtration, washed with methanol and DCM to give the crude compounds of **2a/2b/2c**. The crude was not further purified and directly used for next reaction.

To a 50 mL 3-neck flask was added the **2a/2b/2c** (2.36 mmol), then polyphosphoric acid about 15g was added, the mixture was heated to 140 °C and stirred for 6h. After cooling to room temperature, the mixture was poured to ice-water and neutralized with $NaHCO_3$ and filtered. The precipitate was purified by chromatography, eluted with dichloromethane:petroleum ether (1:1) to obtain the expected product. The 3c was directly used for next reaction and not purified furthermore.

FPPhen: ^{1}H NMR (400 MHz, Chloroform-d) δ 9.60 (d, J = 8.1Hz, 1H), 9.53 (d, J = 8.1Hz, 1H), 9.28 (m, 2H), 8.12 -8.07 (m, 2H), 7.81 (m, 2H), 7.61-7.53 (m, 3H), 7.46 (s, 1H, -CH). HRMS(ESI) calcd for C22H12N4O $[M+H]^+$ 349.10839, found 349.10954.

diBFQ: ^{1}H NMR (400 MHz, Chloroform-d) δ 9.33-9.35 (d, J = 8.0Hz, 1H), 9.27-9.29 (d, J = 8.0Hz, 1H), 8.66-8.68 (d, J=8.0Hz, 2H), 8.07-8.09 (d, J=8.0Hz, 2H), 7.76-7.80 (m, 4H), 7.51-7.58 (m, 3H), 7.45 (s, 1H). HRMS(ESI) calcd for C22H12N4O $[M+H]^+$ 347.11061, found 347.11652.

3c: ^{1}H NMR (400 MHz, Chloroform-d) δ 9.18-9.20 (d, J = 8.0 Hz, 1H), 9.12-9.14 (d, J = 8.0Hz, 1H), 8.69 (s, 2H), 8.06 -8.08 (d, J=8.0Hz, 2H), 7.87-7.89 (d, J = 8.0Hz, 2H), 7.52-7.59 (m, 3H), 7.51 (s, 1H).

Synthesis of dP-diBFQ

3,6-dibromo-11-phenyldibenzo[f,h]furo[2,3-b]quinoxaline (0.368g, 1 mmol), (4-isopropylphenyl)boronic acid (0.49 g, 3 mmol), K_2CO_3 (5.5 mL, 2N) and $Pd(PPh_3)_4$ (0.035 g, 0.12 mmol) were added to 30 ml toluene. Then the reaction mixture was stirred at 120℃ under a nitrogen atmosphere until TLC revealed complete conversion of the starting material. The mixture was cooled, diluted with H_2O and filtered. The residue was purified by silica gel column chromatography (CH_2Cl_2/petroleum ether) to give expected product.

dP-diBFQ: ^{1}HNMR (400 MHz, DMSO-d6) δ 9.21 (d, J = 8.5 Hz, 1H), 9.15-9.09 (m, 3H), 8.18-8.13 (m, 2H), 8.06 (d, J = 8.5Hz, 2H), 8.00 (s, 1H), 7.94-7.87 (m, 4H), 7.64-7.54 (m, 3H), 7.44-7.38 (m, 4H), 2.96 (m, 2H, -CH-), 1.26 (d, J = 7.0 Hz, 12H, 2-CH_3). ^{13}CNMR (400 MHz, Chloroform-d) δ 161.77, 154.64, 148.70, 148.64, 141.66, 141.48, 139.75, 138.69, 138.64, 136.37, 131.38, 130.94, 130.64, 129.17, 129.07, 127.62, 127.15, 126.69, 125.90, 125.82, 121.02, 101.47. HRMS(ESI) calcd for C42H32N2O $[M+H]^+$ 583.27439, found 583.27441. Anal.calcd for C42H32N2O (%): C: 86.57, H: 5.88, N:4.81. Found: C: 86.71%, H:5.86%, N: 4.92%.

Figures

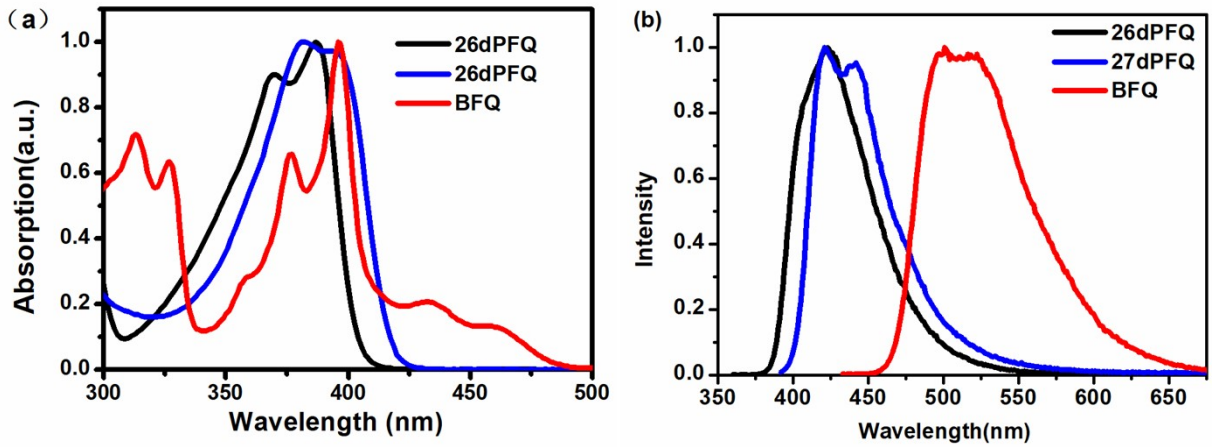


Figure S1 the uv (a) and PL (b) spectra for 26dPFQ, 27dPFQ and BFQ in CH_2Cl_2 solution.

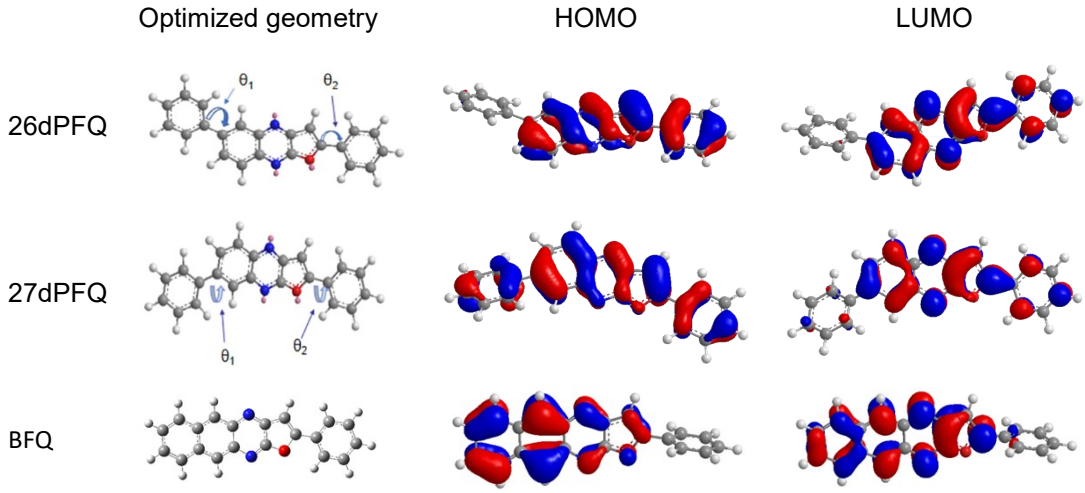
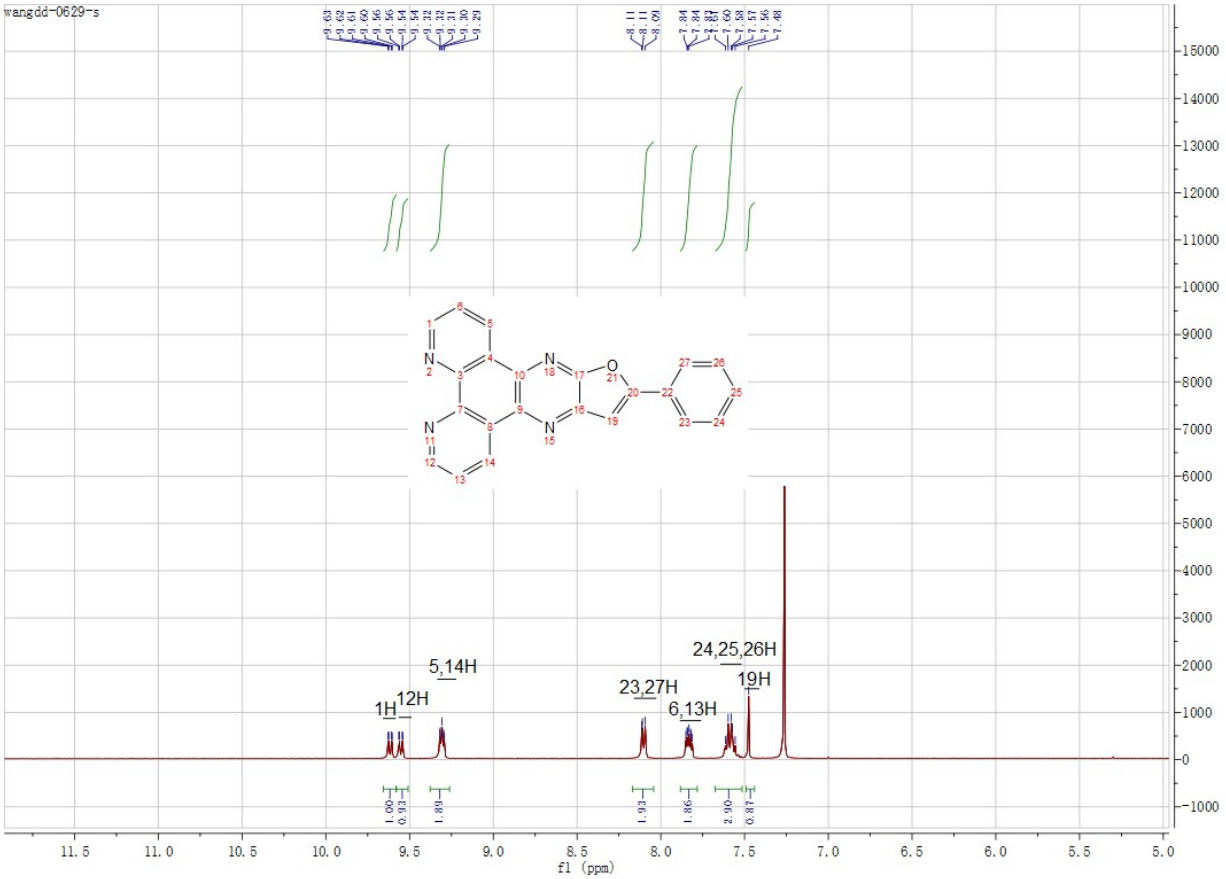


Figure S2 the calculated optimized molecular geometry, electron distribution of HOMO and LUMO orbitals of 26dPFQ, 27dPFQ and BFQ.

Section 3: ^{1}H NMR spectra



FigureS3 ^{1}HNMR spectrum of FPPhen

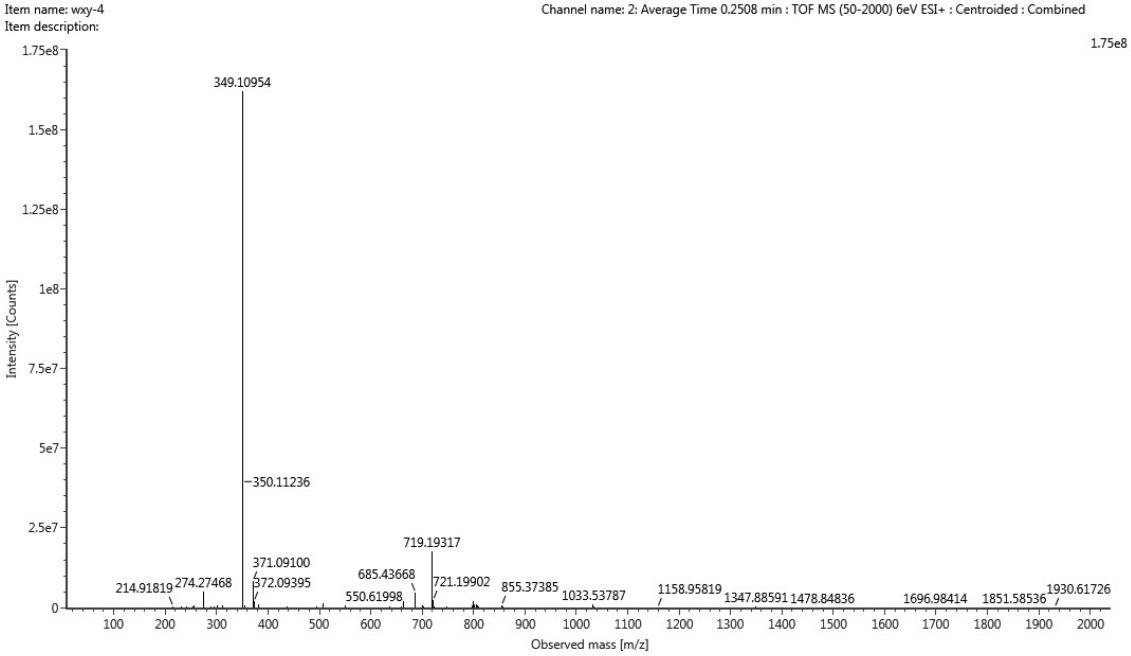
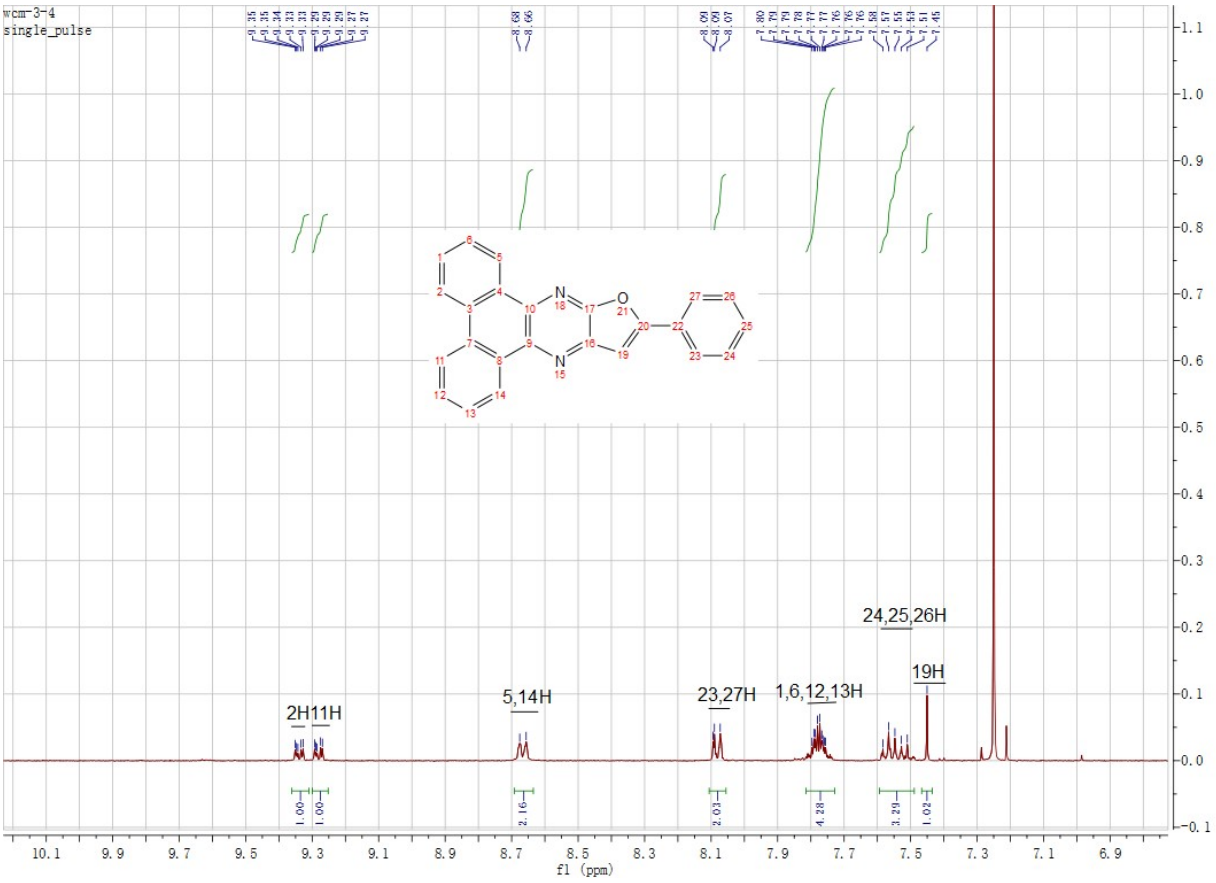
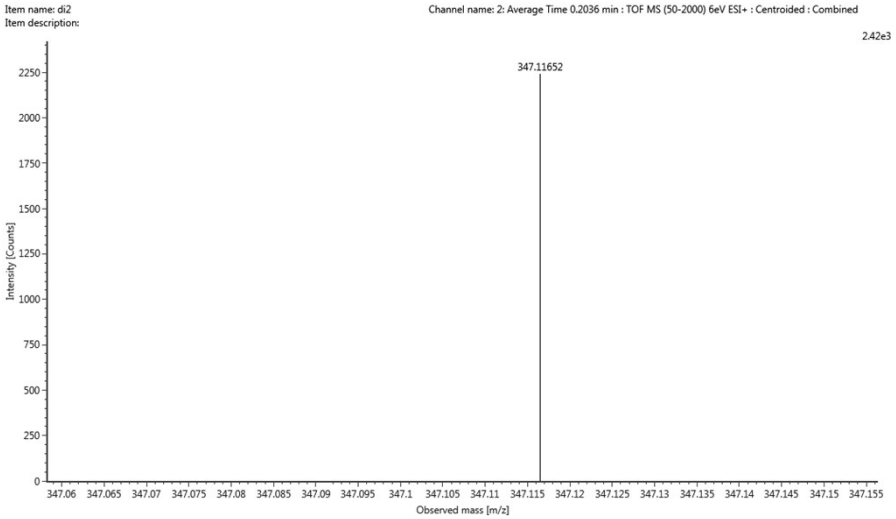


Figure S4 HRMS spectrum of FPPhen



FigureS5 [1]HNMR spectrum of diBFQ



FigureS6 HRMS spectrum of diBFQ

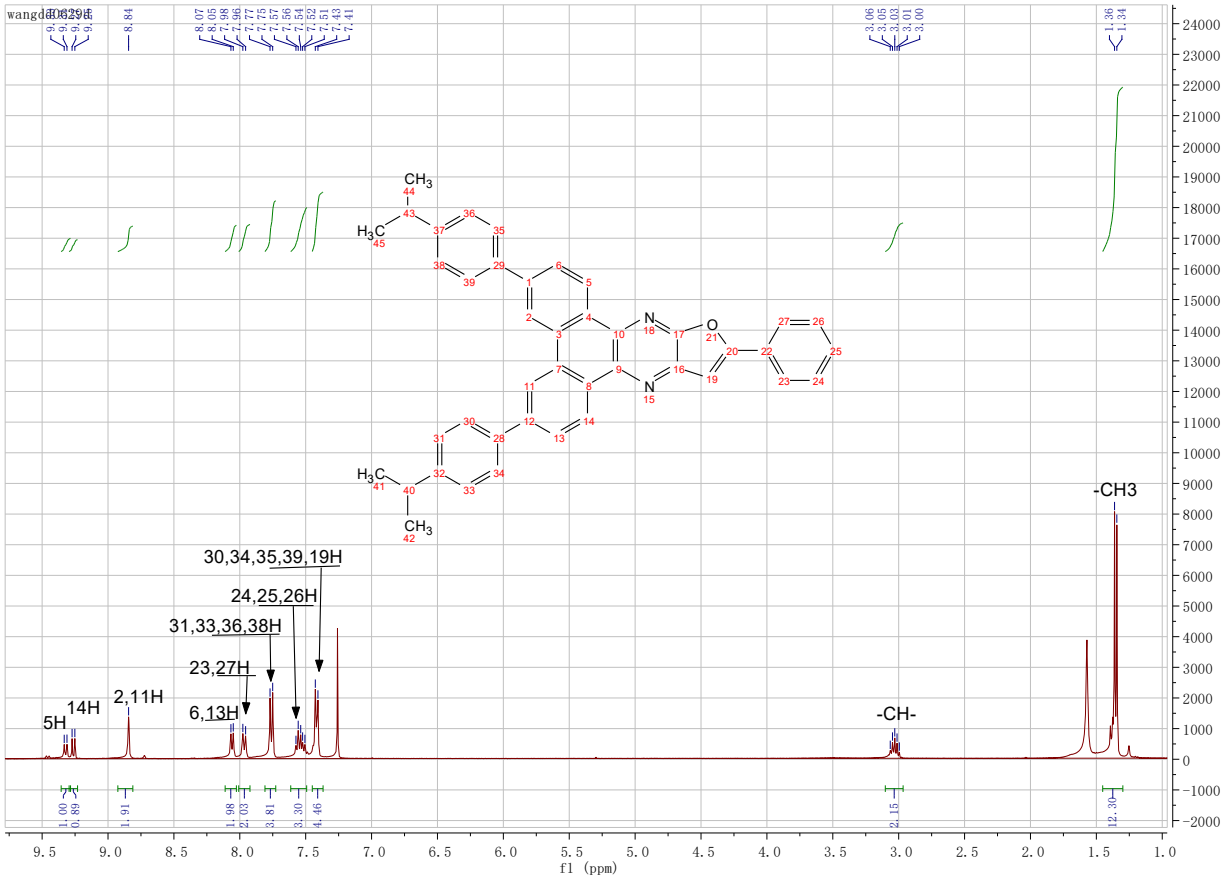


Figure S7 [1]HNMR spectrum of dP-diBFQ

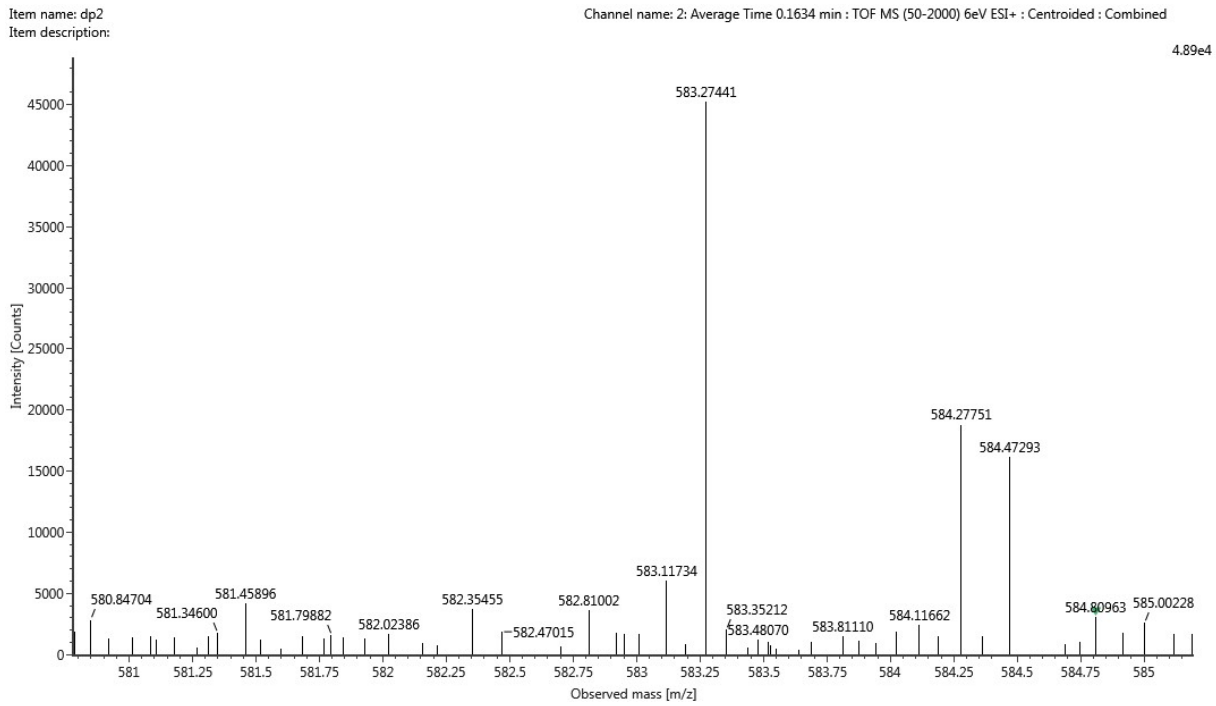


Figure S8 [1]HRMS spectrum of dP-diBFQ

REFERENCE

[1] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V.Bakken, C. Adamo, J. Jaram illo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Revision C.01, Gaussian, Inc., Wallingford CT, 2010.

[2] Liu, W.; Wang, F.; Dai, D.; Li, L.; Dolg, M. The Beijing Four-Component Density Functional Program Package (BDF) And Its Application to EuO, EuS, YbO and YbS. *Theor. Chem. Acc.* **1997**, *96*, 75-83.

[3] Liu, W.; Hong, G.; Li, L. The Beijing Density Functional (BDF) Program Package: Methodologies and Applications, *J. Theor. Comput. Chem.* **2003**, *2*, 257-272.

[4] Hirao, K.; Ishikawa, Y. Recent Advances in Computational Chemistry, World Scientific, Singapore, **2004**, *5*, p257.

[5] Li, Z.; Xiao, Y.; Liu, W. On the Spin Separation of Algebraic Two-Component Relativistic Hamiltonians. *J. Chem. Phys.* **2012**, *137*, 154114.