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Supporting Information

Conformation-controlled Emission of AIE Luminogen: A Tetraphenylethene Embedded Pillar[5]arene Skeleton

Bin Han,[a] Linpeng Zhu,[a] Xi Wang,[a] Ming Bai,*[a] and Jianzhuang Jiang*[b]

[a] *Marine College，Shandong University (Weihai)，Weihai, 264209, China，E-mail: ming_bai@sdu.edu.cn*

[b] *Beijing Key Laboratory for Science and Application of Functional Molecular and Crystalline Materials, Department of Chemistry, University of Science and Technology Beijing, Beijing, 100083, China. E-mail: jianzhuang@ustb.edu.cn*

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Experimental Procedures

General Remarks. Tetrahydrofuran (THF) was distilled from sodium wire and benzophenone under nitrogen. Column chromatography was carried out on a silica gel column (Qingdao Haiyang, 200-300 mesh) with the indicated eluents. 5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetramethoxycalix[4]-arenewas prepared according to the precious report.[14] All the other reagents such as benzophenone, *n*-butyllithium in hexane (2.5 mol/L), and 1,4-dicyanobutane were used as received.

^{1}H NMR spectra were recorded on a Bruker DPX 400 spectrometer (^{1}H: 400 MHz, ^{13}C: 100 MHz) in $CDCl_3$ unless otherwise stated. Spectra were referenced internally using the residual solvent resonances (δ = 7.28 for ^{1}H NMR) relative to $SiMe_4$ (δ = 0 ppm). ^{13}C NMR spectra were referenced internally by using the solvent resonances (δ = 77.00 ppm for $CDCl_3$). Electronic absorption spectra were recorded on a Hitachi U-2900 spectrophotometer. Fluorescence spectra were recorded on a Hitachi F-7000 spectrophotometer. Fluorescence images were taken on a Nikon Eclipse Ti florescence microscope. ESI-MS spectrum was taken on a Thermo Fisher Q-Exactive mass spectrometer. Single-crystal X-ray diffraction analyses were performed on an Aglient Super Nova Atlas Dual diffractometer using Cu*Kα* radiation (λ = 1.54184 Å). Structure was solved by direct methods using SHELXTL and refined by full-matrix least-squares on F^2 using SHELX-97. Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Hydrogen atoms were placed in calculated positions with isotropic displacement parameters set to 1.2×U_{eq} of the attached atom. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited in the Cambridge Crystallographic Data Center with CCDC Number: **EtP5A-DPE**1571969 and **DCB** ⊂**EtP5A-DPE**1572442.

*Synthesis of **EtP5A-DPE**.* To a solution of **EtP5A** (2.67 g, 3 mmol) in dry THF (20 mL), 5.4 mL of 2.5 M solution of *n*-butyllithium in hexane (13.5 mmol) was added at 0°C under nitrogen. The resulting orange-red solution was stirred for 45 min at this temperature. Benzophenone (4.37 g, 24 mmol) was then added and the reaction mixture warmed to room temperature and then stirred at 70^{o}C for another 24 h. The reaction was quenched by adding 10% aqueous ammonium chloride solution. The organic layer was extracted with dichloromethane (3×50 mL), and the combined organic layers were washed with a saturated brine solution and dried over anhydrous $MgSO_4$. The solvent was evaporated, and the resulting crude alcohol was dissolved in 80 mL of toluene in a 150 mL round-bottom flask fitted with a Dean-Stark trap. *p*-Toluenesulphonic acid (190 mg, 1 mmol) was added, and the mixture was refluxed for 4 h and cooled to room temperature. The toluene layer was washed with 10% aqueous NH_4Cl solution and dried over anhydrous $MgSO_4$. After evaporating the solvent, the crude product was purified by silica gel column chromatography using hexane/CH_2Cl_2 (95/5, v/v) as eluent to give white solid in 30% yield (0.49 g).^{1}H NMR (400 MHz, $CDCl_3$), (TMS, ppm): 7.07 (m, 10H, ArH), 6.79 (s, 2H, ArH), 6.75 (s, 2H, ArH), 6.59 (s, 2H, ArH), 6.36 (s, 2H, ArH), 6.15 (s, 2H, ArH), 3.87-3.74 (m, 20H, -OCH_2-), 3.56 (d, 4H, *J* = 6.8 Hz, -$ArCH_2$-), 3.08 (S, 4H, -$ArCH_2$-), 1.55-1.09 (m, 30H, CH_3). ESI-MS: Found an isotopic cluster peaking at m/z [M+Na$^+$] 1077.5490; Calculated for $C_{68}H_{78}O_{10}Na$, 1077.5493.

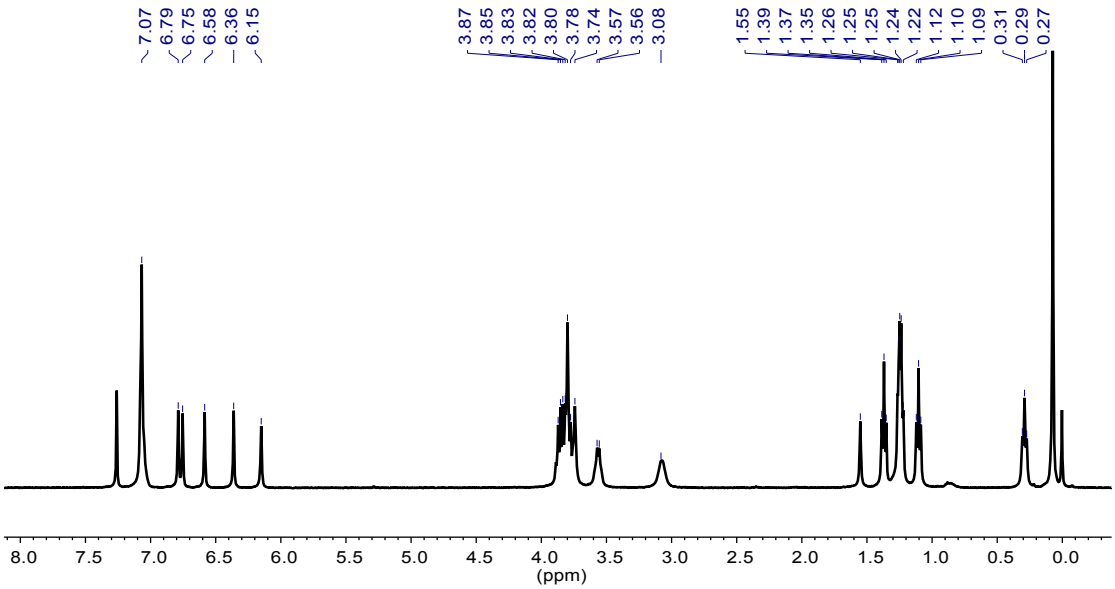


Fig. S1 ^{1}H NMR spectrum of compound **EtP5A-DPE** in $CDCl_3$.

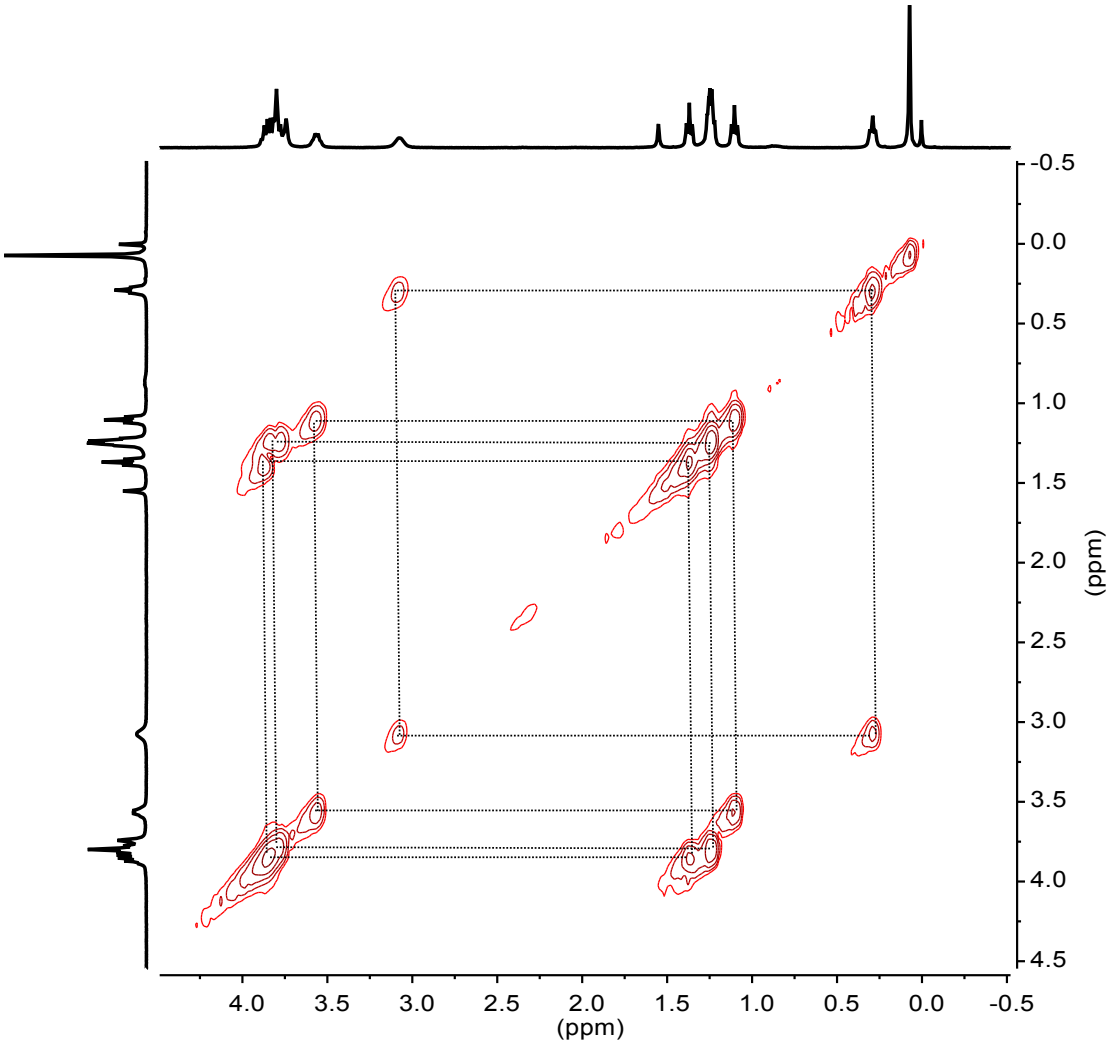


Fig. S2 2D COSY spectrum of compound **EtP5A-DPE** in $CDCl_3$.

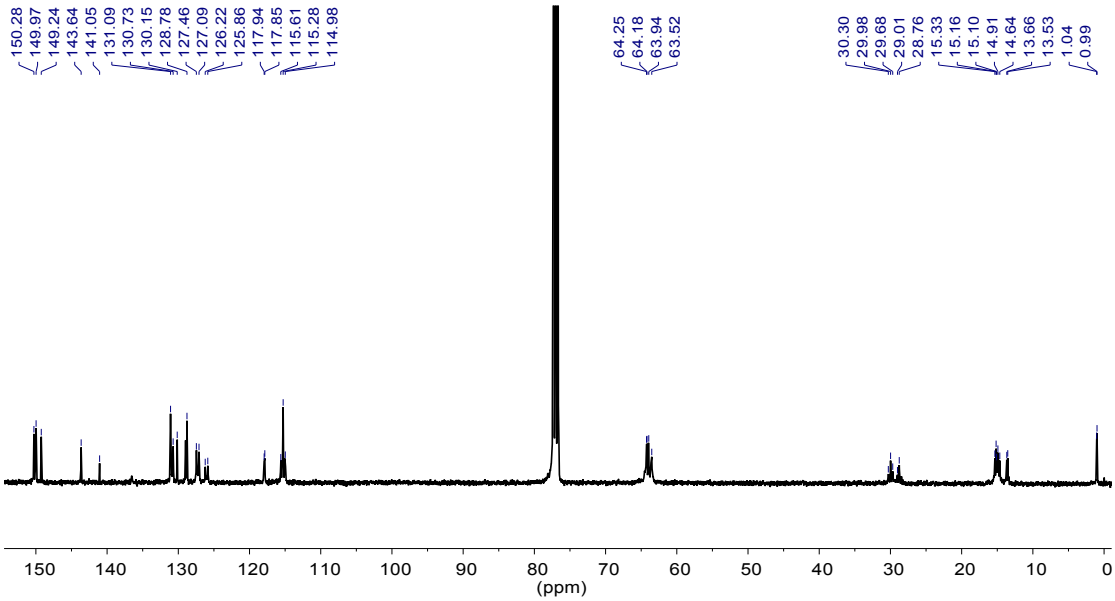


Fig. S3 ^{13}C NMR spectrum of compound **EtP5A-DPE** in $CDCl_3$.

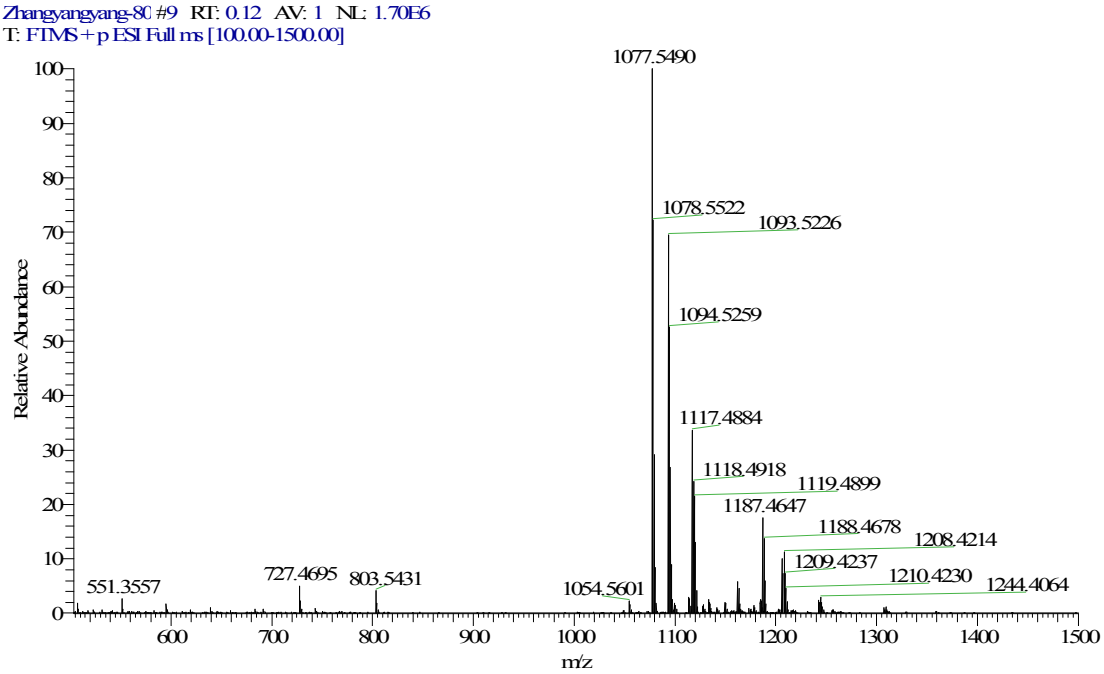
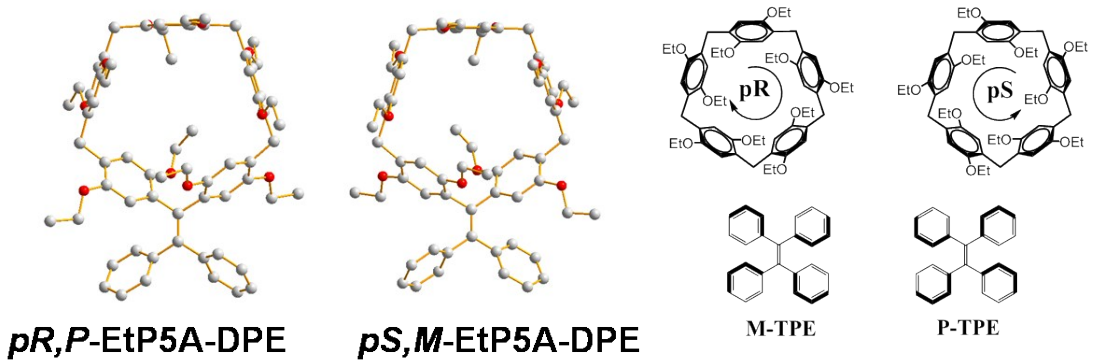


Fig. S4 ESI-MS spectrum of compound **EtP5A-DPE.**



***pR,P*-EtP5A-DPE** ***pS,M*-EtP5A-DPE**

Fig. S5 The rules for nominations of the two conformational enantiomers of **EtP5A-DPE**. The compound **EtP5A-DPE** possesses two asymmetric factors in crystal state. One is the exhibit planar chirality for the pillar[5]arene (*pR* and *pS*), the other is propeller-shaped chirality (*P* and *M*) for achiral TPE twisting in one direction which can take two chiral conformations.

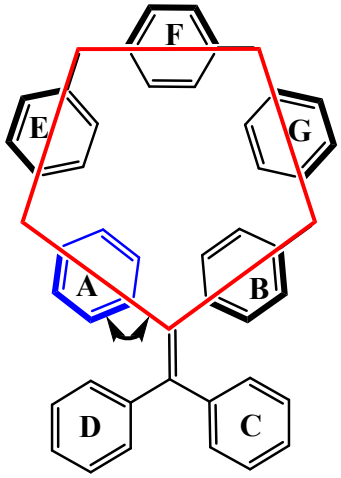


Fig. S6 The definition of the dihedral angles formed between the phenyl rings of the pillar[5]arene and the plane constructed by the five *meso* carbon.

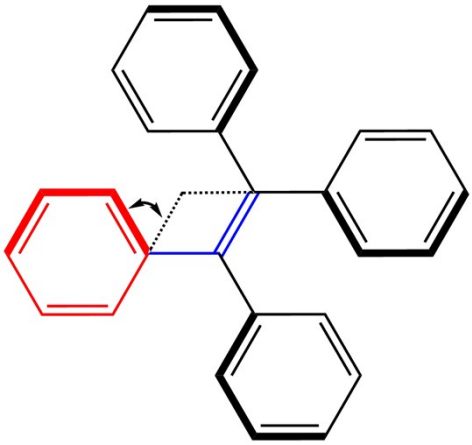


Fig. S7 The definition of the dihedral angles formed between the phenyl rings and the C = C bond.

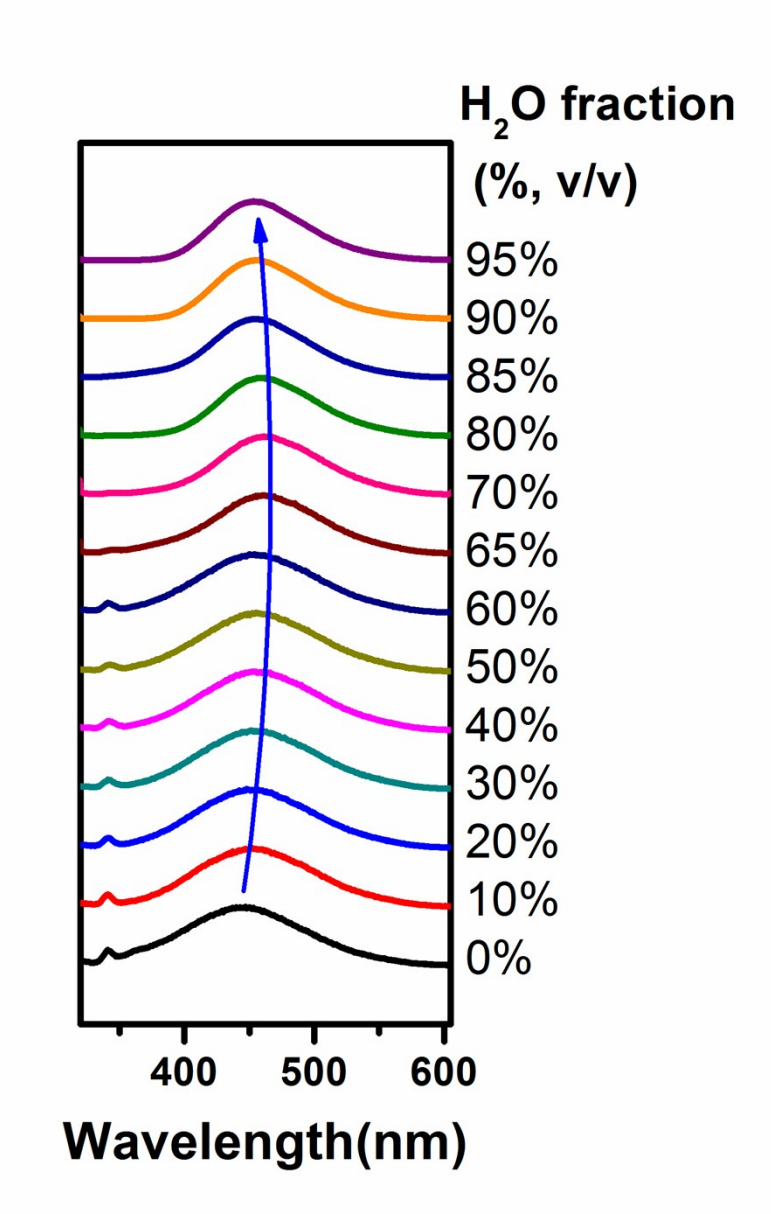


Fig. S8 Normalized fluorescence spectra of **EtP5A-DPE** in THF-water mixtures with different water fractions. Concentration: 20 μM; λ_{ex}: 310 nm (5 nm, 5 nm); 293K.

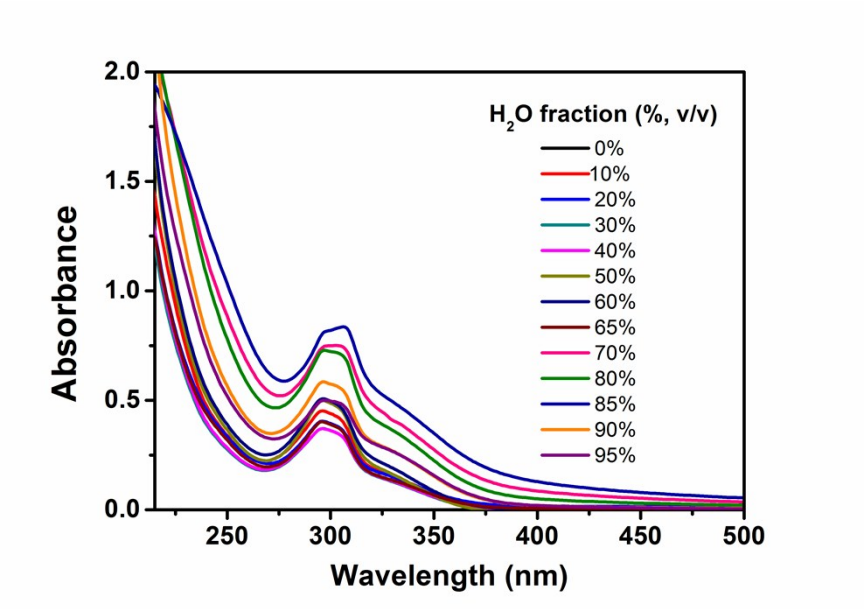


Fig. S9 Uv-vis spectra of **EtP5A-DPE** in THF-H_2O mixtures with different water fractions. Concentration: 20 μM.

Table S1 The table of reported perethyl pillar[5]arene torsion angles.

	Torsion Angles				
CCDC 831701[20]	87.774	89.494	89.328	89.655	89.787
CCDC 831702[20]	87.238	89.258	89.262	84.000	84.081
CCDC 852484[21]	89.359	88.601	89.754	89.358	89.847
CCDC 850074[22]	89.079	87.968	88.136	86.791	88.035
CCDC 995204[23]	88.519	89.739	89.823	87.097	87.973
CCDC 1052604[24]	88.277	88.113	89.608	88.373	86.806

Table S2 The table of the pillar[5]arene torsion angles of **EtP5A-DPE** and **DCB⊂EtP5A-DPE**.

Ring	***pR,P*-EtP5A-DPE**	***pS,M*-EtP5A-DPE**	**DCB⊂*pR,P*-EtP5A-DPE**	**DCB⊂*pS,M*-EtP5A-DPE**
A	53.200°	61.663°	85.635°	85.211°
E	81.677°	84.930°	84.035°	88.815°
F	84.417°	84.417°	88.821°	88.821°
G	84.930°	81.677°	88.815°	84.035°
B	61.663°	53.200°	85.211°	85.635°

Table S3 The table of the dihedral angles formed between the phenyl rings and the C = C bond.

Ring	***pR,P*-EtP5A-DPE**	***pS,M*-EtP5A-DPE**	**DCB⊂*pR,P*-EtP5A-DPE**	**DCB⊂*pS,M*-EtP5A-DPE**
A	66.324°	54.409°	86.898°	63.457°
B	51.932°	47.285°	85.370°	68.424°
C	47.285°	51.932°	68.424°	85.370°
D	54.409°	66.324°	63.457°	86.898°