Electronic Supplementary Information

Guest-induced emission enhancement in the permanent porous conjugated carboracycle crystal

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Materials

Commercially available reagents used without purification

1,2-Bis(4-bromophenyl)ethyne (Tokyo Chemical Industry Co., Ltd)
Decaborane ($B_{10}H_{14}$) (Toronto Research Chemicals)
Silver(I) nitrate ($AgNO_3$) (Fujifilm Wako Pure Chemical Corporation)
Bis(1,5-cyclooctadiene)nickel(0) ($Ni(cod)_2$) (Fujifilm Wako Pure Chemical Corporation)
2,2'-Bipyridyl (Tokyo Chemical Industry Co., Ltd)
1,5-Cyclooctadiene (cod) (Tokyo Chemical Industry Co., Ltd)

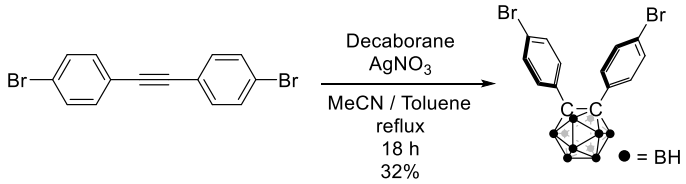
Commercially available solvents used without purification

Toluene, deoxidized (Fujifilm Wako Pure Chemical Corporation)
MeCN, super dehydrated (Fujifilm Wako Pure Chemical Corporation)
$CHCl_3$ (Fujifilm Wako Pure Chemical Corporation)
n-hexane (Fujifilm Wako Pure Chemical Corporation)
CH_2Cl_2 (DCM) (Fujifilm Wako Pure Chemical Corporation)
MeOH (Fujifilm Wako Pure Chemical Corporation)
N,N-Dimethylformamide (DMF), deoxidized (Fujifilm Wako Pure Chemical Corporation)
AcOEt (Fujifilm Wako Pure Chemical Corporation)
1,2-Dichloroethane (DCE) (Fujifilm Wako Pure Chemical Corporation)
1,2-Dibromoethane (DBE) (Tokyo Chemical Industry Co., Ltd)
1-Bromo-2-chloroethane (BCE) (Tokyo Chemical Industry Co., Ltd)
Butane(C_4H_{10}) (Charged in cylinder, Tokyo Chemical Industry Co., Ltd)
$CDCl_3$ (Eurisotop)

Synthetic Experiments

Synthetic experiments were performed under dry N_2 atmosphere with typical Schlenk technique unless otherwise noted. An MBRAUN glovebox system, UNIlab, was used for treating air-unstable reagent. Pure water was supplied with Merck Elix Essential UV 3 water purifier. ^{1}H, $^{13}C\{^{1}H\}$ and $^{11}B\{^{1}H\}$ NMR spectra were recorded on a JEOL JNM-ECZ400 and JNM-ECZ400S FT-NMR instrument at 400, 100, and 128 MHz, respectively. The ^{1}H and ^{13}C chemical shift values were expressed relative to tetramethylsilane (TMS) (0.00 ppm) as an internal standard. The ^{11}B chemical shift values were expressed relative to $BF_3 \cdot Et_2O$ (0.00 ppm) as an external standard. Analytical thin-layer chromatography (TLC) was performed with silica gel 60 Merck F254 plates. Column chromatography was performed with Wakogel® C-300 silica gel. High-resolution mass spectrometry (HRMS) spectra were obtained on a Thermo Fisher Scientific Exactive Plus for atmospheric pressure chemical ionization (APCI). HRMS were performed at the Technical Support Office (Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University)

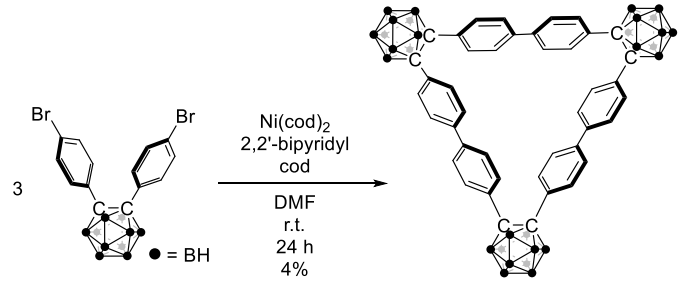
1,2-Bis(4-bromophenyl)-*o*-carborane



Scheme S1. Synthetic scheme of 1,2-bis(4-bromophenyl)-*o*-carborane

1,2-Bis(4-bromophenyl)ethyne (2.689 g, 8.0 mmol), decaborane (1.102 g, 9.0 mmol) and $AgNO_3$ (0.270 g, 1.6 mmol) were added to a 100 mL 2-neck round bottom flask. To the flask, toluene (40 mL) and MeCN (5.0 mL) were added under N_2 atmosphere, and the mixture was refluxed at 110 °C for 18 h. After filtration and evaporation of the solvents to afford orange solid, the crude was supported by silica in $CHCl_3$ and purified by silica gel column chromatography (eluent: *n*-hexane/DCM = 30/1 (v/v)). Recrystallization from boiling MeOH/$CHCl_3$ afforded colorless crystal of 1,2-bis(4-bromophenyl)-*o*-carborane (1.163 g, 2.6 mmol, 32%). The product was characterized by ^{1}H NMR analysis according to the literature.[1]

CB3Ph6



Scheme S2. Synthetic scheme of **CB3Ph6**

To a 300 mL round bottom flask, 1,2-bis(4-bromophenyl)-*o*-carborane (1.135 g, 2.50 mmol), $Ni(cod)_2$ (1.374 g, 5.00 mmol), 2,2'-bipyridyl (0.194 g, 1.24 mmol), and DMF (150 mL) were added in an MBRAUN glovebox system under N_2 atmosphere. The flask was capped with septum and taken out from glovebox. To the flask, cod (0.50 mL, 4.07 mmol) was added, and the mixture was stirred at room temperature for 24 h. To the resultant mixture, pure water (ca. 200 mL) was added. Brown precipitate was collected by vacuum filtration and extracted with $CHCl_3$ concentrated with rotary evaporator to afford brown solid. The crude solid was purified by silica gel column chromatography (eluent: *n*-hexane/AcOEt = 5/1 (v/v)). Recrystallization was performed by vapor diffusion method: filtrated DCE solution of the semi-purified solid and MeOH vapor. The colorless co-crystal of **CB3Ph6** and DCE (34 mg, 0.03 mmol, 4%) was obtained by vacuum filtration. The reaction proceeded in unsatisfactory yield probably because of forming large quantities of precipitation, which might be oligomerized or polymerized products. The soluble component was purified and characterized. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.45 (d, J = 8.4 Hz, 12H), 7.32 (d, J = 8.4 Hz, 12H), 3.8–1.6 (br, 30H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) = 139.8, 131.1, 130.6, 126.3, 84.70. $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ (ppm) = −2.90 , −10.49. HRMS (APCI) calcd. for $C_{42}H_{54}B_{30}Cl^-$ $[M+Cl]^-$ 923.6824, found 923.6806.

Preparation of crystalline samples

All samples were stored under air at room temperature.

DCE@CB3Ph6: Recrystallization by slow evaporation of DCE solution at rt.

CB3Ph6α: Vacuum drying of **DCE@CB3Ph6** at 100 °C for 3 h.

Details of solid-vapor adsorption experiments

Solid-vapor adsorption of **CB3Ph6**α was performed with DCE, DBE, or BCE vapors under ambient pressure for several hours at rt.

Details of solid-gas adsorption experiments

Solid-gas adsorption of **CB3Ph6**α was performed with butane gas under ambient pressure for overnight at rt.

Single-Crystal X-ray Diffraction Analysis

The X-ray crystallographic analysis was carried out with a Rigaku Saturn 724+ with MicroMax-007 HF CCD diffractometer with Varimax Mo optics using graphite-monochromated Mo Kα radiation. The structures were solved with SHELXT 2015[2] and refined on F^2 with SHELXL 2015[3] on Olex 2-1.2[4] and Shelxle.[5] All hydrogen atoms were placed at calculated positions and refined using a riding model. The program *Mercury 2020.3.0*[6] and *ORTEP-3*[7] was used to generate the X-ray structural diagram. Crystalline sample of **DCE@CB3Ph6** for this study is prepared by vapor diffusion of MeOH into DCE solution at −30 °C, followed by slow evaporation of the solvent at rt.

Table S1. Crystallographic data.

Compound name	**DCE@CB3Ph6**	**DBE@CB3Ph6**
CCDC number	2495493	2495494
Empirical formula	$C_{26}H_{28}B_{10}\cdot C_2H_4Cl_2$	$C_{26}H_{28}B_{10}\cdot C_2H_4Br_2$
Formula weight	982.10	1071.02
Temperature / K	143(2)	143(2)
Wavelength / Å	0.71075	0.71075
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/c	*C*2/c
a / Å	7.2450(12)	7.2884(17)
b / Å	31.353(5)	31.271(7)
c / Å	23.751(4)	23.733(6)
α / °	90	90
β / °	91.880(3)	92.054(3)
γ / °	90	90
V / Å^3	5392.1(15)	5406(2)
Z	4	4
ρ / g cm^{-3}	1.210	1.316
a / cm^{-1}	0.156	1.535
F(000)	2024	2168
θ range / °	3.038–27.460	3.026–27.485
Limiting indices	$-9\le h\le 9$ $-39\le k\le 36$ $-22\le l\le 30$	$-9\le h\le 9$ $-40\le k\le 40$ $-29\le l\le 30$
Collected unique reflections	21828/6058	21870/6128
R_{int}[a]	0.0456	0.0411
S (Goodness-of-fit on F^2)[b]	1.586	1.082
R_1 [$I > 2\sigma(I)$][c]	0.1211	0.0807
wR_2 (all data)[d]	0.3971	0.2454

[a] $R_{int} = \Sigma||F_o|^2-<|F_o|^2>|/\Sigma|F_o|^2$ [b] $S = [\{\Sigma w(|F_0|^2-|F_c|^2)^2\}/(N_o - N_p)]^{1/2}$ [c] $R_1 = [\Sigma(|F_0|^2-|F_c|^2)^2/\Sigma(|F_0|^2)^2]^{1/2}$

[d] $wR_2 = [\Sigma w(|F_0|^2-|F_c|^2)^2/\Sigma w(|F_0|^2)^2]^{1/2}$. $w = 1/[\sigma^2(|F_0|^2)+[(ap)^2+bp]]$, where $p = [|F_0|^2+2|F_c|^2]/3$

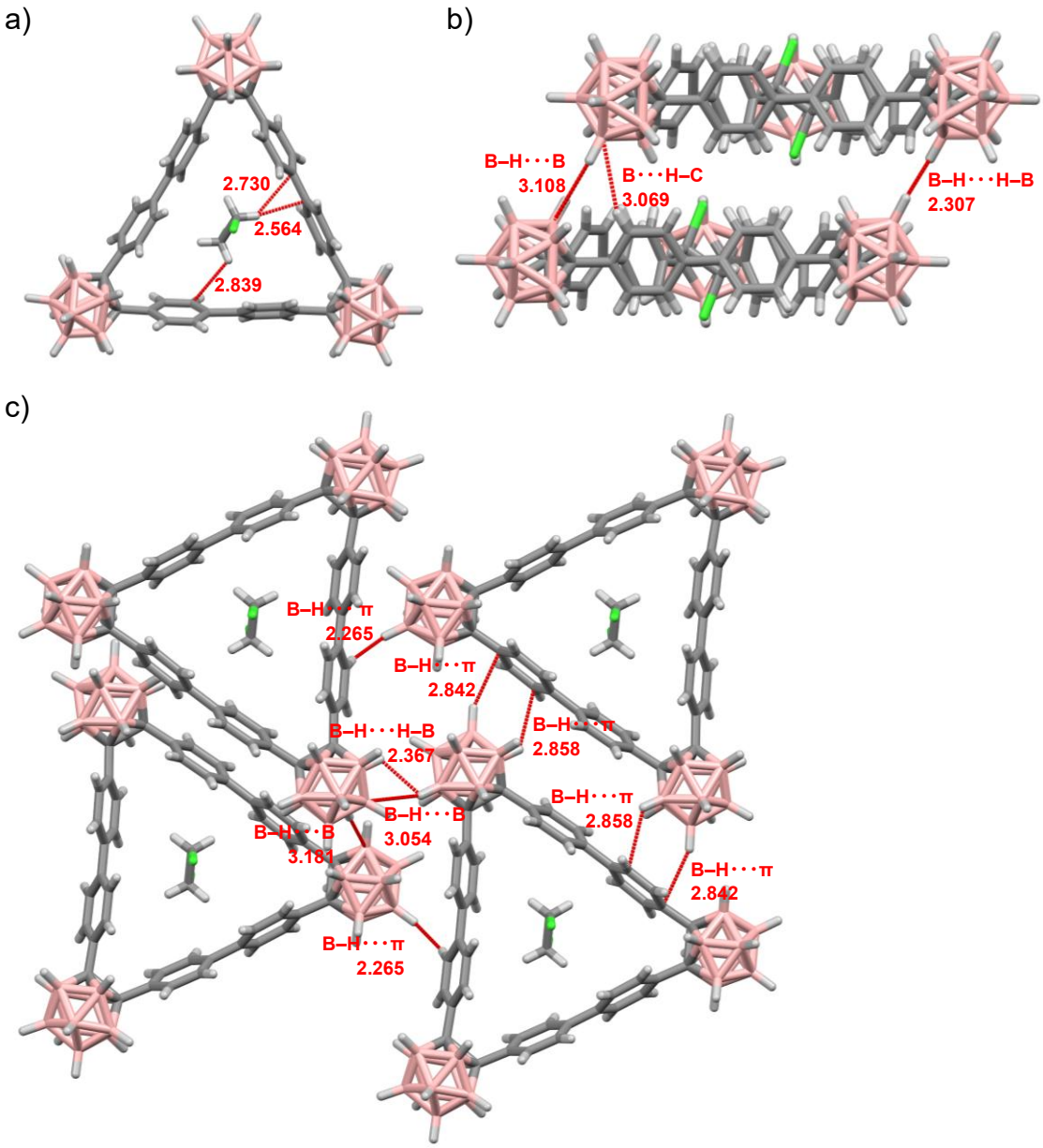


Figure S1. Single-crystal structure of **DCE@CB3Ph6** with highlighted short contacts (< sum of vdW radii, distance in angstrom) including a) **CB3Ph6** and DCE (C–H···π), b) **CB3Ph6** molecules in the same column (B–H···H-B, B–H···B, B···H–C), and c) **CB3Ph6** and DCE molecules in the same layer (B–H···H–B, B–H···B, B–H···π). Colors: C, gray; B, pink; H, white; Cl, green.

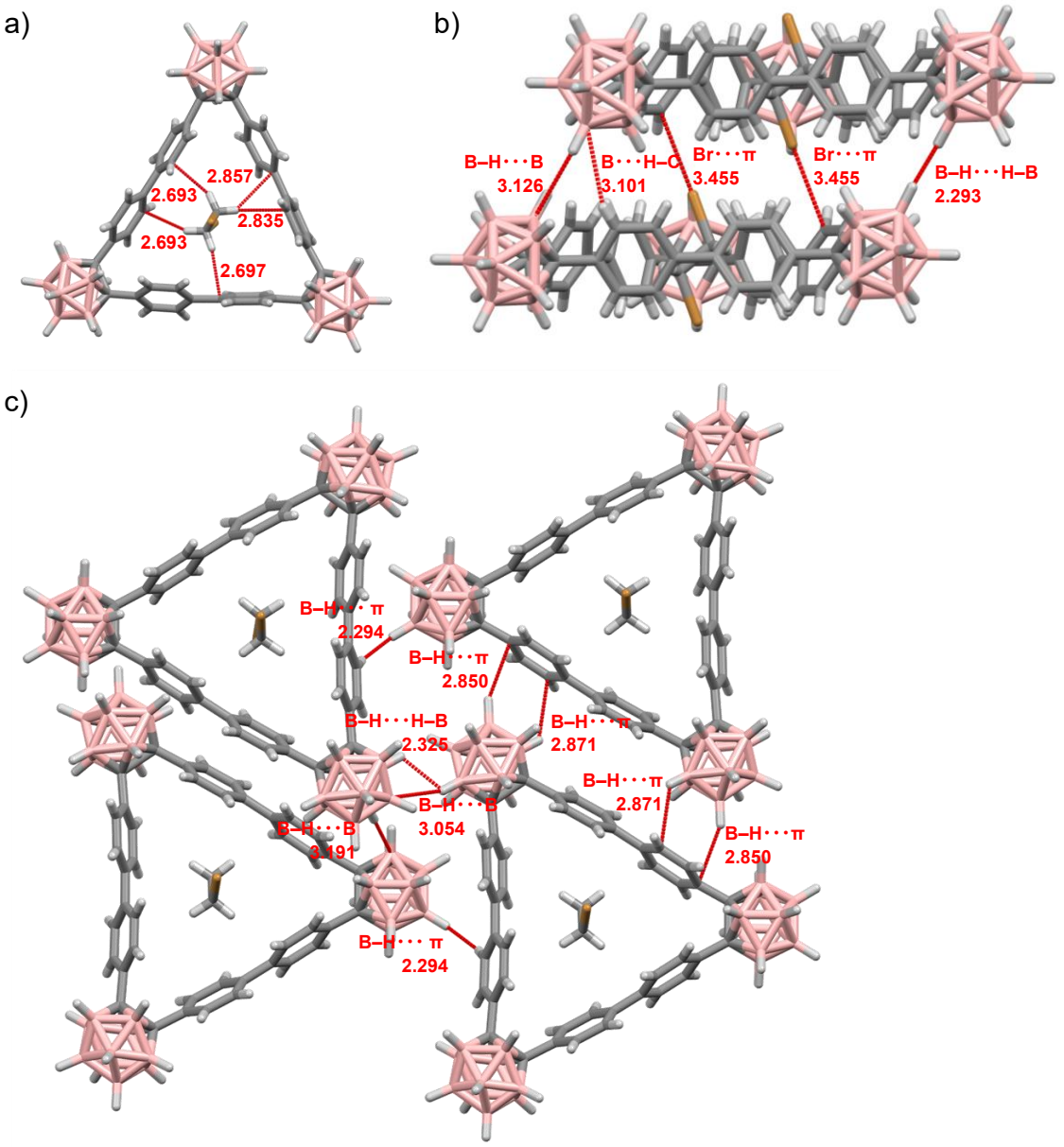


Figure S2. Single-crystal structure of **DBE@CB3Ph6** with highlighted short contacts (< sum of vdW radii, distance in angstrom) including a) **CB3Ph6** and DBE (C–H···π), b) **CB3Ph6** and DBE molecules in the same column (B–H···H–B, B–H···B, B···H–C, Br···π), and c) **CB3Ph6** and DBE molecules in the same layer (B–H···H–B, B–H···B, B–H···π). Colors: C, gray; B, pink; H, white; Br, brown.

Powder X-ray Diffraction Analysis

Powter X-ray diffraction (PXRD) data for indexing was obtained using Rigaku SmartLab with a Ge (111) Johannson monochromator (Cu Kα_1 radiation λ=1.54059 Å, 50 kV and 40 mA, transmittance mode), a HyPix-3000 detector, a borosilicate capillary (outside diameter, 0.7 mm; wall thickness, 0.01 mm; sample loading height, ~30 mm), and a capillary rotation attachment. Measurement parameters were set as follows: 2 theta range, 3–50°; step, 0.005°; speed, 0.5°/ min; rotation speed, 120 rpm. The analysis was carried out with the powder X-ray diffraction analysis software SmartLab Studio II (Rigaku). Indexing programs DICVOL[8] or ITO[9] were used for the determination of cell dimensions. The diffraction profiles were decomposed with the whole powder pattern fitting (WPPF) method. Following these data, corresponding space groups were determined based on systematic extinctions. Fitting parameters for the indexing were defined as follows:

$$R_{\mathrm{wp}} = \left\{ \frac{\sum_{\mathrm{i}} w_{\mathrm{i}} [y_{\mathrm{i}} - f_{\mathrm{i}}(x)]^2}{\sum_{\mathrm{i}} w_{\mathrm{i}} {y_{\mathrm{i}}}^2} \right\}^{\frac{1}{2}}$$

$$R_{\mathrm{p}} = \frac{\sum_{\mathrm{i}} |y_{\mathrm{i}} - f_{\mathrm{i}}(x)|}{\sum_{\mathrm{i}} y_{\mathrm{i}}}$$

$$R_{\mathrm{e}} = \left(\frac{N - P}{\sum_{\mathrm{i}} w_{\mathrm{i}} {y_{\mathrm{i}}}^2} \right)^{\frac{1}{2}}$$

$$S = \frac{R_{\mathrm{wp}}}{R_{\mathrm{e}}}$$

in which y_{i} is a diffraction intensity, $f_{\mathrm{i}}(x)$ is a calculated diffraction intensity, P is a parameter for the least-squares method, w_{i} is a statistical weight and N is the number of data points.

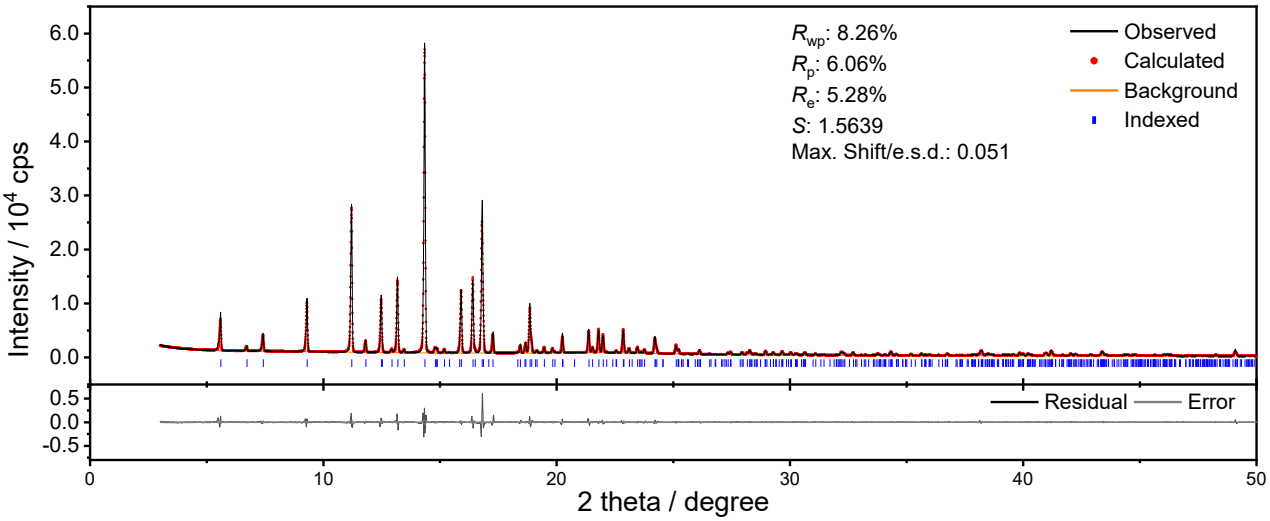


Figure S3. WPPF profile of **CB3Ph6**α with indexing (monoclinic, *C*2/c, a = 7.2500(3) Å, b = 31.5201(12) Å, c = 24.6332(10) Å, α = 90.000°, β = 105.0753(8)°, γ = 90.000°). Parameters were almost identical with SCXRD result of **DCE@CB3Ph6** (monoclinic, *C*2/c, a = 7.2450(12) Å, b = 31.353(5) Å, c = 23.751(4) Å, α = 90°, β = 91.880(3)°, γ = 90°), which indicates limited rearrangement of the structure upon DCE removal. Slight change in c (+ 0.88 Å) and β (+ 13°) suggests that crystal lattice transformed by a little extent, while overall molecular packing was hardly affected upon DCE removal.

Typical PXRD data were collected with a Rigaku SmartLab Diffractometer (sealed tube (50 kV, 40 mA); Cu Kα, 1.542 Å; Bragg–Brentano geometry). PXRD samples were placed on a single-crystal silicon substrate.

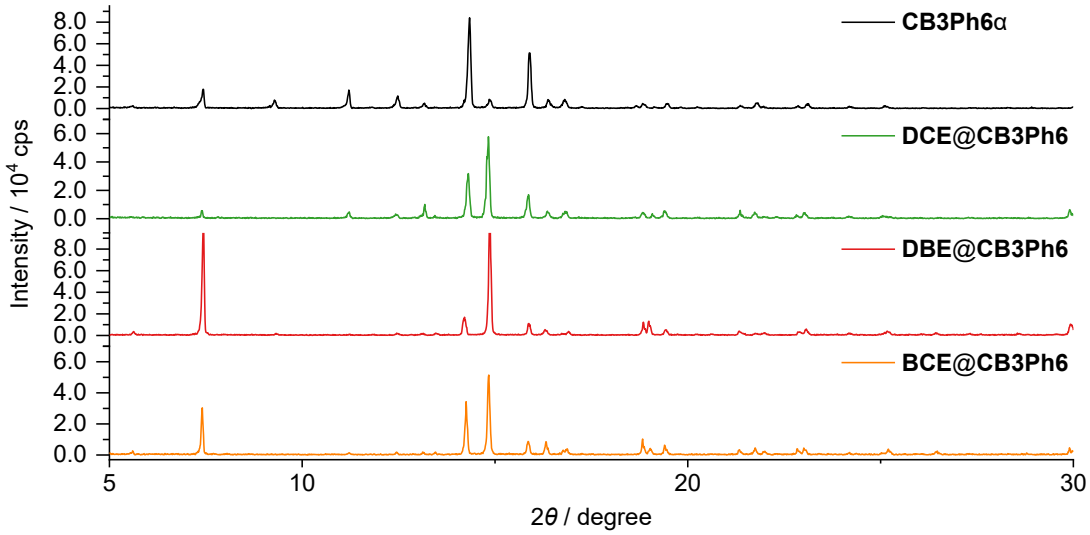


Figure S4. PXRD patterns of **CB3Ph6** crystals with or without vaporous guests.

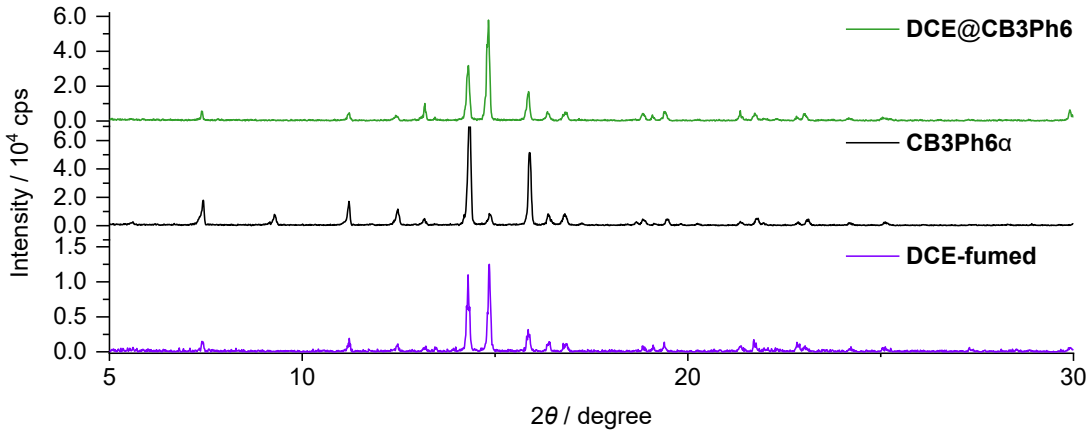


Figure S5. PXRD patterns of **DCE@CB3Ph6**, **CB3Ph6**α, and exposed to DCE vapor after guest removal (**DCE-fumed**). The correspondence of the patterns between **DCE@CB3Ph6** and **DCE-fumed** supported the recovery of DCE uptake by solid-vapor adsorption.

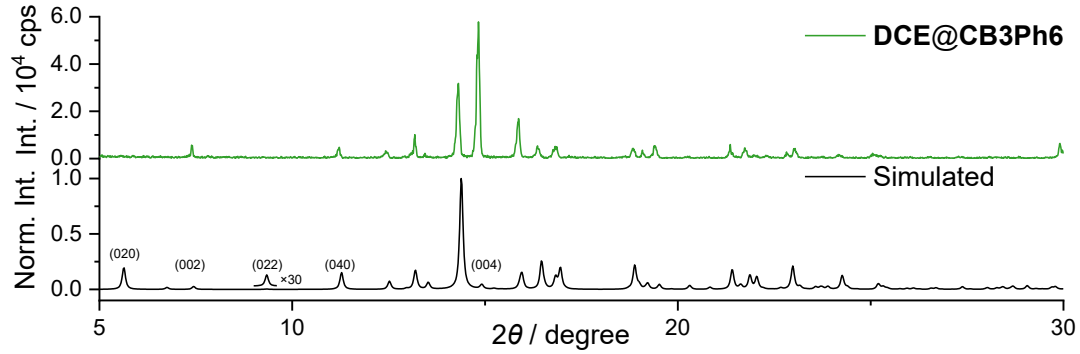


Figure S6. PXRD experimental and partially indexed simulated patterns of **DCE@CB3Ph6**. Due to the crystal orientation on the diffraction substrate, diffraction intensity from (020) and (040) planes was weakened, while that from (002) and (004) was magnified. Taking the orientation into consideration, correspondence of peak positions ensured sufficient semi-single-crystallinity of the bulk crystals.

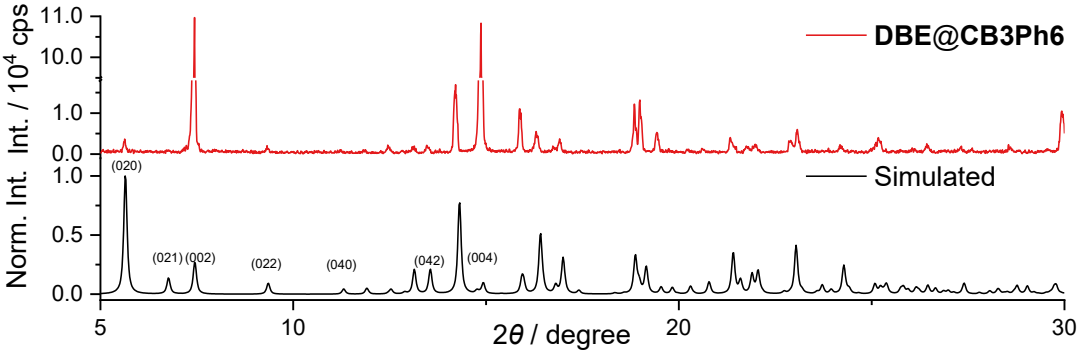


Figure S7. PXRD experimental and partially indexed simulated patterns of **DBE@CB3Ph6**. Due to the crystal orientation on the diffraction substrate, diffraction intensity from (020) and (040) planes was weakened, while that from (002) and (004) was magnified. Taking the orientation into consideration, correspondence of peak positions ensured sufficient semi-single-crystallinity of the bulk crystals.

Adsorption Properties

Gas and vapor sorption isotherms were obtained using a BELSORP-max (BEL Japan Inc., Osaka, Japan) sorption analyzer at room temperature. The equilibrium points were determined if the pressure change for 300 s is less than 0.3% of the pressure gauge values. Sample was activated by overnight heating at 80 °C under vacuum.

Surface area of the material was calculated by Brunauer-Emmett-Teller (BET) theory.[10,11] The following equation was used at standard temperature and pressure (STP).

$$\frac{P}{V(P_0 - P)} = \frac{1}{CV_m} - \frac{C - 1}{CV_m} \cdot \frac{P}{P_0}$$

,where V is the weight of adsorbate per unit mass at a given relative pressure, P is equilibrium pressure of adsorbate, P_0 is saturation pressure of adsorbate, C is BET constant, and V_m is monolayer adsorbate volume per unit mass. Experimental adsorption data was subjected to linear fitting of $P/V(P_0-P)$ vs P/P_0 plot in the range where C is positive. Then, V_m was calculated by the following equation with the slope (s) and intercept (i) values obtained from fitting.

$$V_m = \frac{1}{s + i}$$

Finally, the specific surface area per unit mass (S_{BET}) was calculated by the following equation:

$$S_{BET} = \frac{V_m N_A \sigma}{M_V}$$

,where N_A is Avogadro's number (= 6.02×10^{23} molecules/mol), σ is cross-sectional area of the adsorbate (= 0.162 nm^2 for N_2), and M_v is the molar volume of adsorbate (= 22414 cm^3).

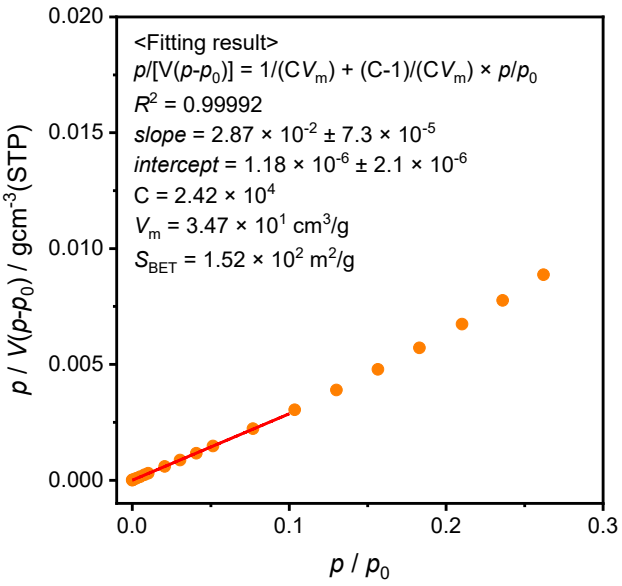


Figure S8. BET surface area plot of **CB3Ph6α** to N_2 at 77 K. Orange scatters and red line represent experimental data and fitting result, respectively.

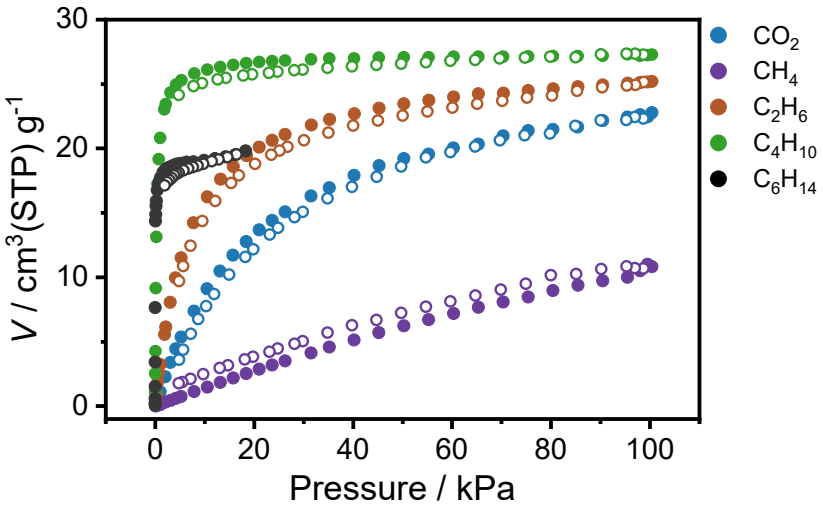


Figure S9. CO_2 and alkane sorption isotherms of **CB3Ph6**α recorded at 298 K. Solid and open circles represent adsorption and desorption, respectively.

Thermal Analysis

Thermogravimetric analyses (TGA) were performed by a HITACHI STA 7200RV instrument with an aluminum pan and a heating rate of 10 °C/min up to 550 °C under nitrogen flow (200 mL/min). Differential scanning calorimetry (DSC) measurements were carried out on a HITACHI DSC 7020 instrument with an aluminum pan and a heating rate of 10 °C/min under nitrogen flow (50 mL/min).

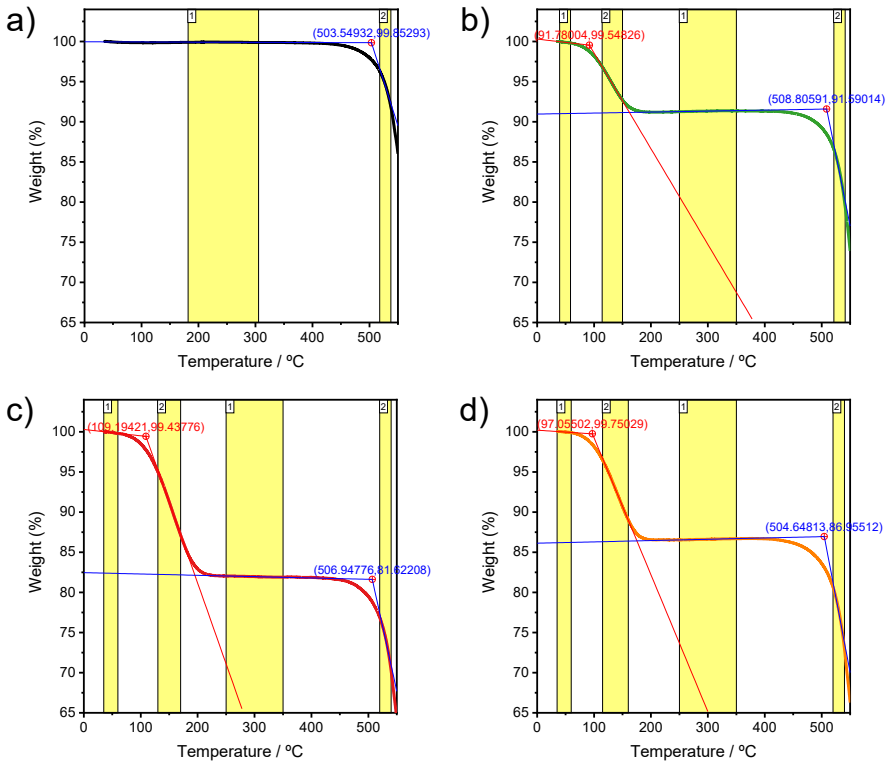


Figure S10. TGA thermograms of a) **CB3Ph6**α, b) **DCE@CB3Ph6**, c) **DBE@CB3Ph6**, and d) **BCE@CB3Ph6** analyzed by extrapolation to obtain guest release and decomposition temperature labeled as red and bule intersections with (x,y) coordinates. *Onset Of Slope* add-in implemented in *OriginPro 2020* software was used for analysis.

Table S2. Summary of host–guest ratio and thermal properties of the crystals

Crystals	Solvent : **CB3Ph6** (TGA) [a]	Solvent : **CB3Ph6** (NMR) [b]	T_{sol} / °C [c]	T_d / °C [d]
CB3Ph6α	0.00 : 1	0.00 : 1	n.d.	504
DCE@CB3Ph6	0.85 : 1	0.96 : 1	92	509
DBE@CB3Ph6	1.03 : 1	0.99 : 1	109	507
BCE@CB3Ph6	0.95 : 1	1.00 : 1	97	505

[a] Solvent molecules to **CB3Ph6** molar ratio determined by TGA analyses. [b] Solvent molecules to **CB3Ph6** molar ratio determined by ^{1}H NMR analyses. [c] Temperature at which vaporous solvent guests were released. [d] Temperature at which decomposition occurred.

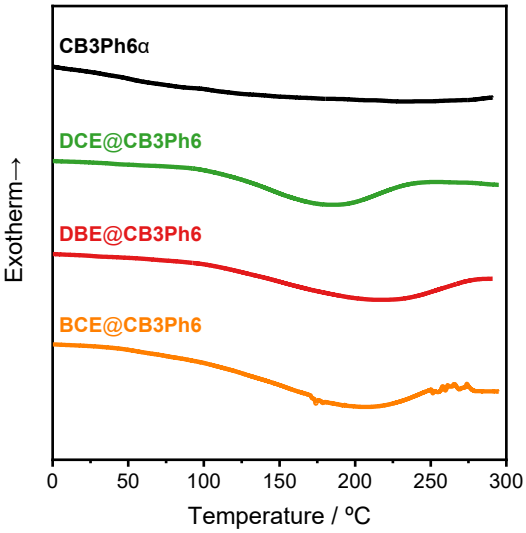


Figure S11. DSC thermograms of **CB3Ph6** crystals: **CB3Ph6**α (black) , **DCE@CB3Ph6** (green), **DBE@CB3Ph6** (red), and **BCE@CB3Ph6** (orange). Endothermic peaks of solvated crystals indicated solvent release from channels.

Variable-temperature PXRD Measurement

Variable-temperature PXRD (VT-PXRD) was carried out by Anton Paar DCS500 while samples were covered with a Graphite dome. Measurements were conducted under N_2 atmosphere. Sample was placed on an Inconel® substrate.

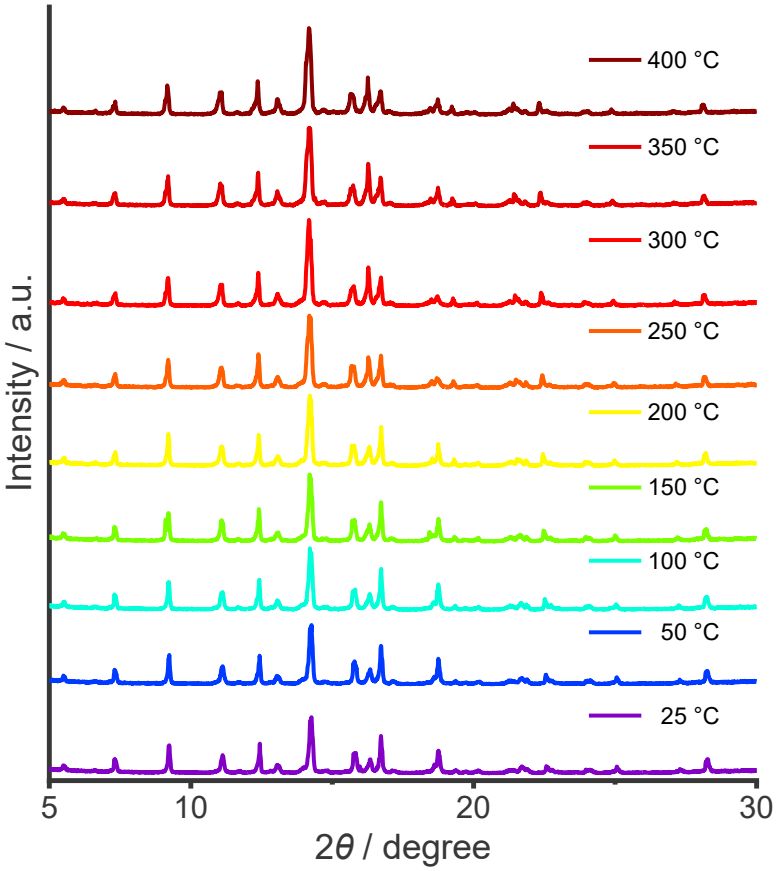


Figure S12. VT-PXRD patterns of **CB3Ph6**α measured at different temperatures up to 400 °C.

Non-covalent Interaction Plot

Non-covalent interaction (NCI) plot was performed by *Multiwfn 3.8* software.[12]

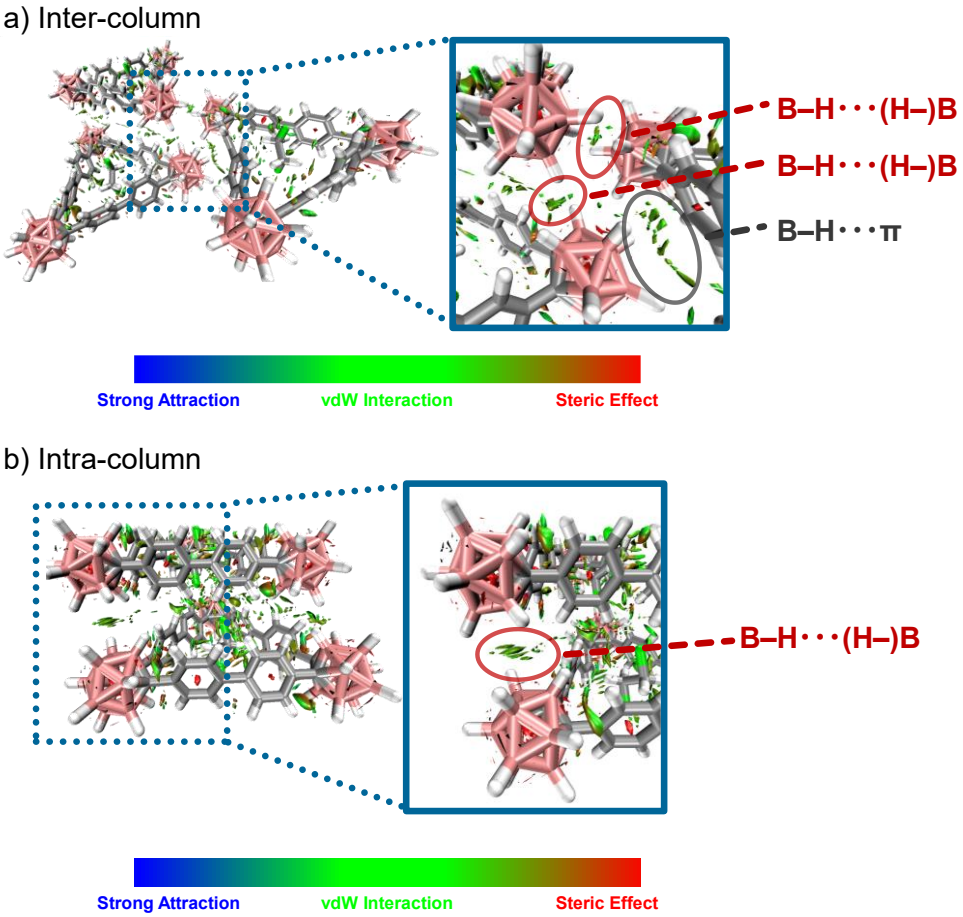


Figure S13. Isosurfaces of **DCE@CB3Ph6** in a) inter- and b) intra-column of 1D array calculated by NCI plot representing the intermolecular interactions (isovalue = 0.6).

Optical Properties

UV–vis absorption spectra were obtained on a SHIMADZU UV3600i plus spectrophotometer. Photoluminescence (PL) spectra were measured with a HORIBA JOBIN YVON Fluorolog-3 spectrofluorometer and an Oxford Optistat DN for temperature control. The fluorescence quantum yield (QY) was recorded on a HAMAMATSU Quantaurus-QY Plus C13534-01 model. The PL lifetime measurement was performed on a HORIBA Deltaflex spectrofluorometer system with a UV diode laser (DeltaDiode 375 nm). Spectroscopic measurements were performed at room temperature unless otherwise noted. Solvents guaranteed as spectroscopic grade were used for the measurements.

Table S3. Summary of solution-state optical properties.

Solvent[a]	λ_{abs} / nm	λ_{PL} / nm[b]	Φ_{PL}[b,c]	τ_{PL} / ns[d]	τ_{PL}^{ave} / ns[e]	χ^2	k_r / ns^{-1}[f]	k_{nr} / ns^{-1}[g]
$CHCl_3$	276	485	0.007	6.0 (39%), 1.5 (46%), 0.3 (15%)	1.1	1.28	0.0064	0.90
CH_2Cl_2	276	503	–	–	–	–	–	–
MeCN	274	569	–	–	–	–	–	–

[a] Measured in 1.0×10^{-5} M. [b] Excited at λ_{abs}. [c] Absolute quantum yield determined by integrating sphere method. [d] Excited at 375 nm. [e] $\tau_{PL}^{ave} = \Sigma_i \tau_i f_i$, where f_i : relative amplitude of ith component (%), τ_i: luminescent decay lifetime of ith component(s). [f] $k_r = \Phi_{PL}/\tau_{PL}^{ave}$. [g] $k_{nr} = (1-\Phi_{PL})/\tau_{PL}^{ave}$. –: not measured.

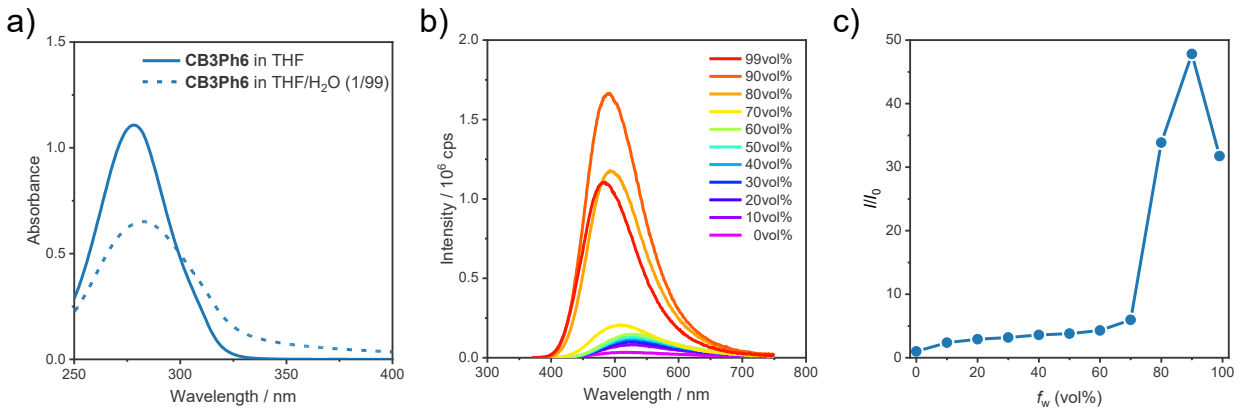


Figure S14. a) UV absorption spectra of **CB3Ph6** in THF solution and THF/H_2O (1/99) mixture. b) PL spectra of **CB3Ph6** in THF/H_2O mixtures with different vol% of water. c) PL intensity ratio of THF/H_2O mixtures compared to that of THF solution. I and I_0 represent PL intensity at the maximum emission wavelength of THF/H_2O mixtures with different volume fraction of H_2O (f_w) and THF solution, respectively. All spectra were obtained under the concentration of 1.0×10^{-5} M. Low energy shoulder in UV absorption spectra indicates aggregate formation of **CB3Ph6** in the THF/H_2O mixture.

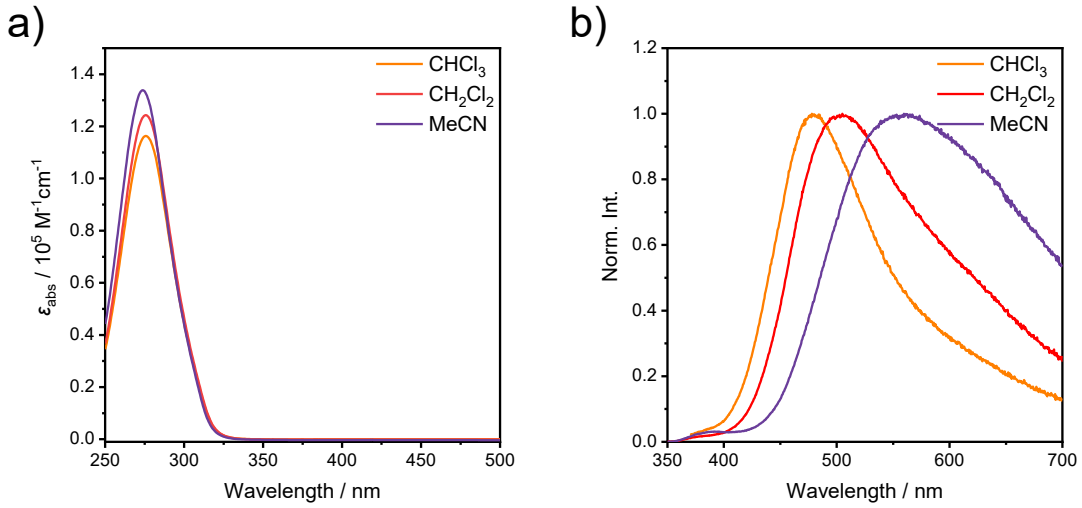


Figure S15. a) UV absorption and b) PL spectra of **CB3Ph6** in solution state (1.0×10^{-5} M). UV absorption spectra showed almost no dependency on solvent polarity, while PL spectra red-shifted by increasing polarity. This indicates excited-state ICT states formed in **CB3Ph6**.

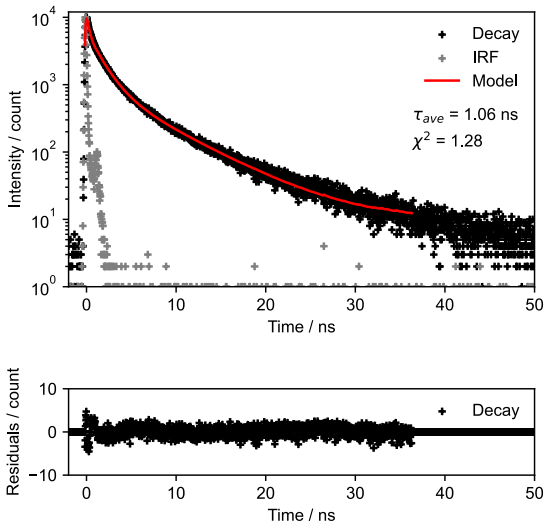


Figure S16. PL decay profiles of **CB3Ph6** in $CHCl_3$ (1.0×10^{-5} M).

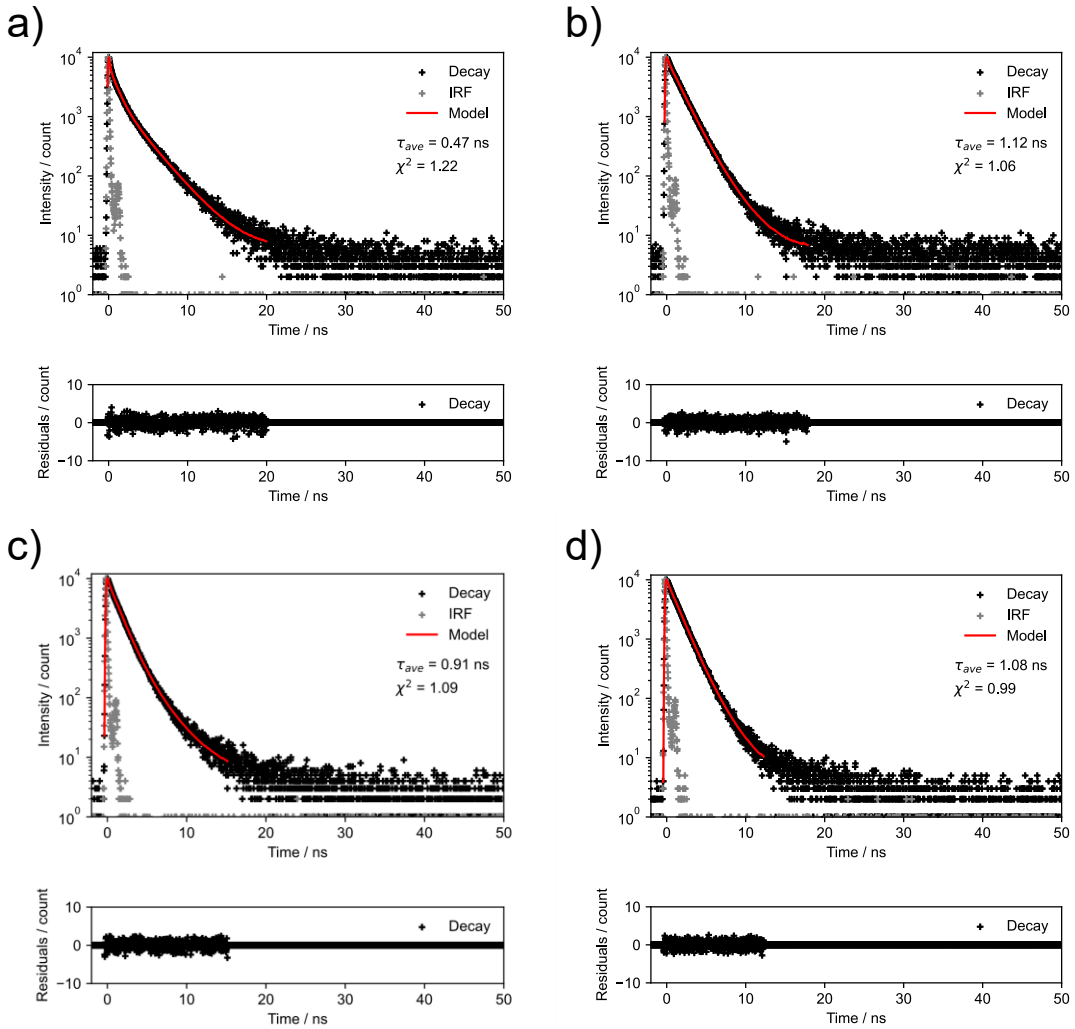


Figure S17. PL decay profiles of a) **CB3Ph6**α, b) **DCE@CB3Ph6**, c) **DBE@CB3Ph6**, and d) **BCE@CB3Ph6**.

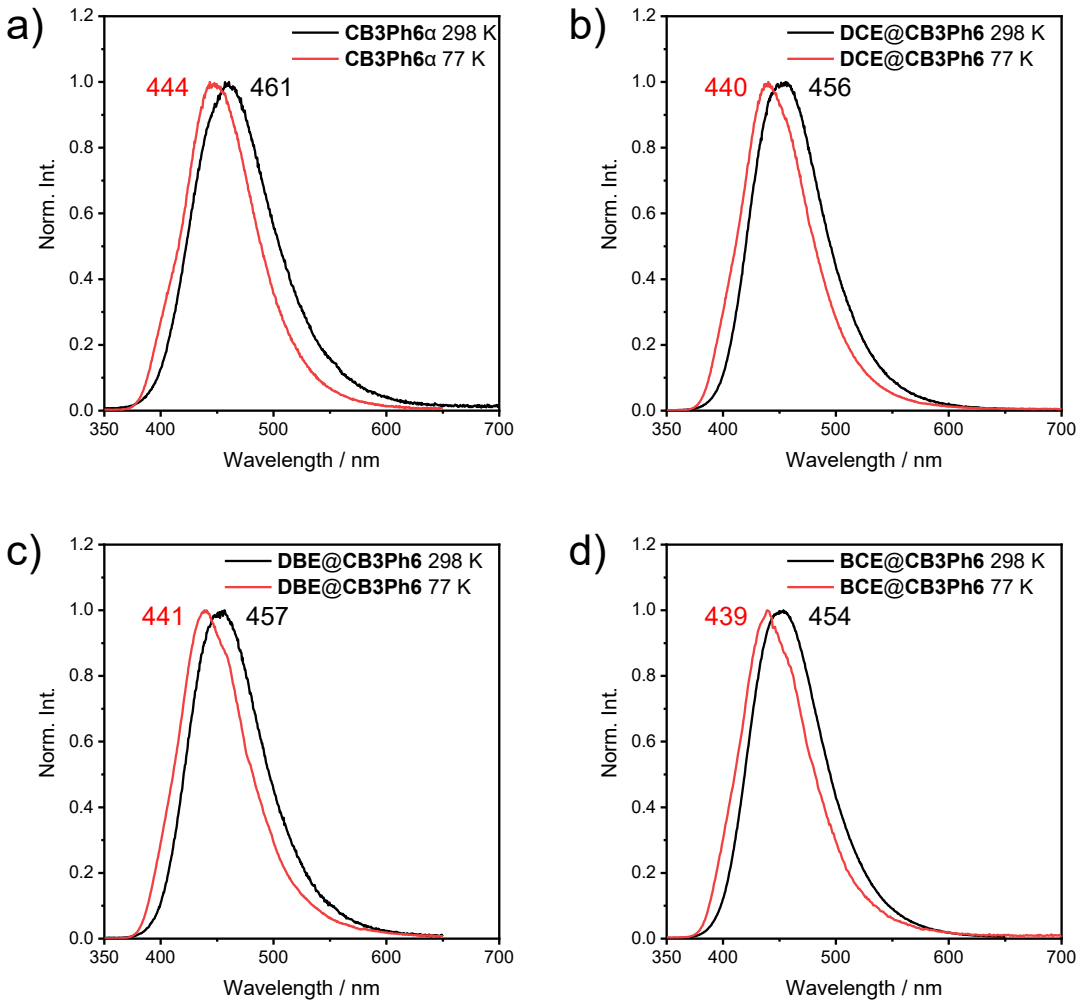


Figure S18. PL spectra measured at 298 K and 77 K of a) **CB3Ph6**α, b) **DCE@CB3Ph6**, c) **DBE@CB3Ph6**, and d) **BCE@CB3Ph6**. The numbers represent maximum emission wavelengths of each spectrum (nm).

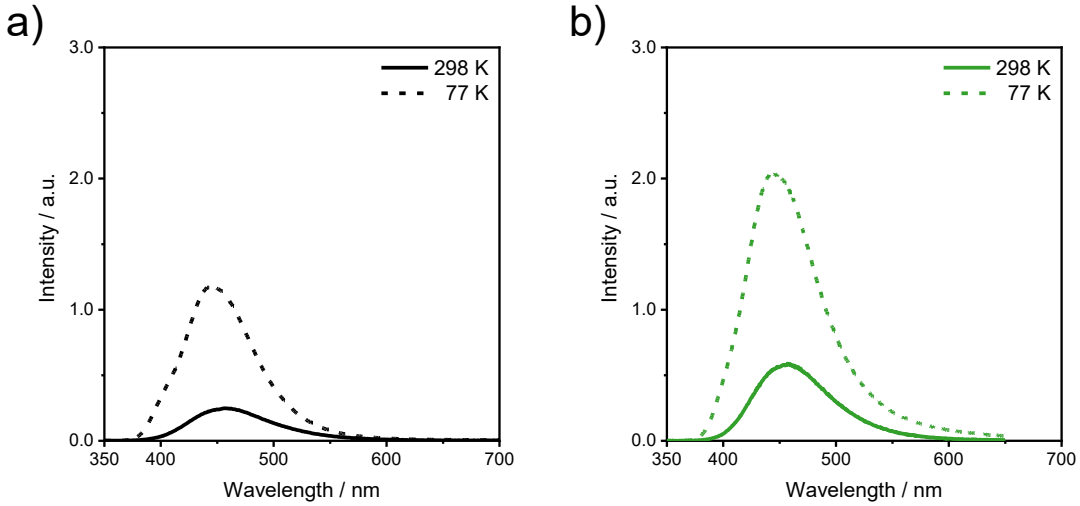


Figure S19. Variable-temperature PL spectra of a) **CB3Ph6**α and b) **DCE@CB3Ph6**.

Theoretical Calculation

General

The Gaussian 16 program Revision C.01 package[13] was used for density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations. B3LYP/6-31+G(d,p) level was used for calculation. Geometry optimization was conducted in ground singlet (S_0) and excited singlet (S_1) states. Optimized structures at S_0 states were obtained for all compounds and confirmed as local minimum on each potential energy surface using frequency calculations. Kohn-Sham orbitals of HOMOs and LUMOs were generated from the optimized structure using GaussView 6 (isovalues: 0.02).

QM/MM calculation

The molecular structures in crystalline state were optimized by the quantum mechanics / molecular mechanics (QM/MM) method. The molecular coordinates for QM/MM analyses were extracted from single-crystal structures. The calculation models were constructed by cut out cluster of 27 molecules from SCXRD structures. The central one molecule in the high layer was calculated at B3LYP /6-31+G(d,p) level and the surrounding molecules in the low layer were dealt in the universal force field with frozen geometry.

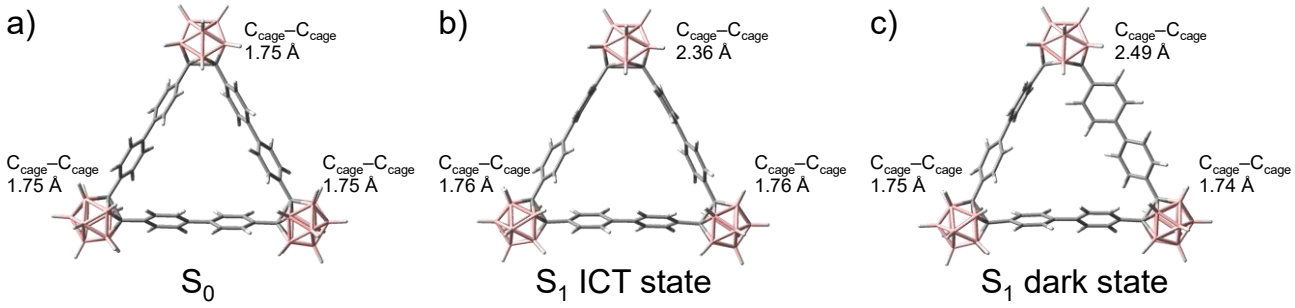


Figure S20. Optimized geometries of a) S_0, b) S_1 ICT, and c) S_1 dark states of isolated **CB3Ph6**. C_{cage}–C_{cage} bond lengths were indicated. B3LYP/6-31+G(d,p) level was used for calculation. (colors: boron, pink; carbon, gray; hydrogen, white)

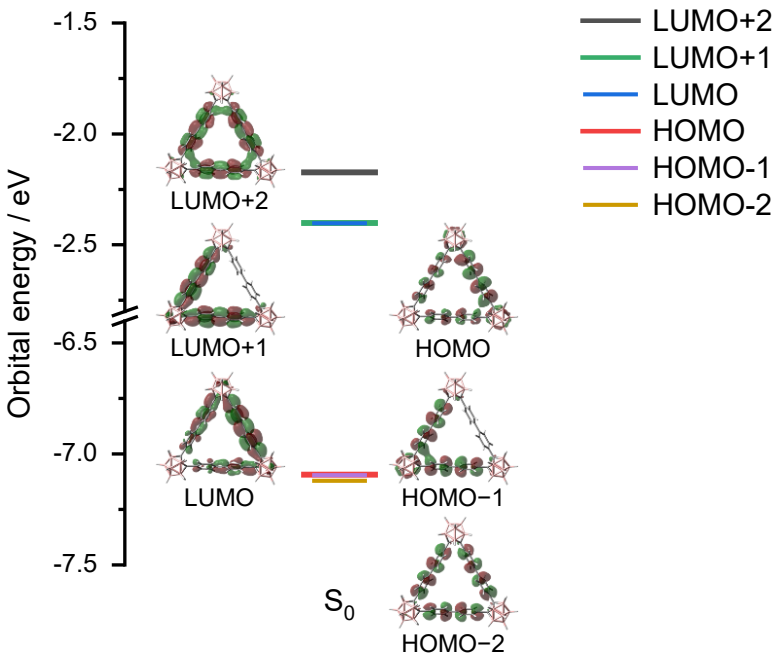


Figure S21. Energy diagram of selected orbitals with corresponding calculated Kohn–Sham frontier orbital distribution of **CB3Ph6** in the S_0 states. Isovalues are 0.02. B3LYP/6-31+G(d,p) level was used. (colors: boron, pink; carbon, gray; hydrogen, white)

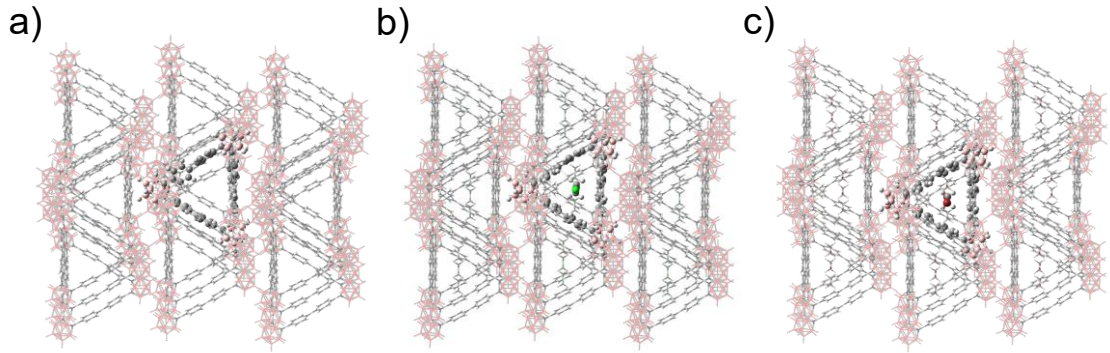


Figure S22. Arrangements of 27 molecules used for constructing QM/MM model of **CB3Ph6**. The central molecule (drawn in ball and stick structure) was treated by QM in high layer and the rest surrounding molecules (drawn in tube structure) were treated by MM in low layer. (colors: boron, pink; carbon, gray; hydrogen, white; chlorine, green; bromine, red)

Table S4. Summary of calculated crystal-state ICT states [a]

Crystal	C_{cage}–C_{cage} / Å	λ_{PL}^{calc} / nm [b]	Oscillator strength (*f*)
CB3Ph6α	2.36, 1.77, 1.76	480	0.30
DCE@CB3Ph6	2.35, 1.76, 1.76	476	0.31
DBE@CB3Ph6	2.34, 1.76, 1.75	474	0.29
BCE@CB3Ph6	–	–	–

[a] Calculated by QM/MM method. [b] Calculated emission wavelength. –: Not calculated due to the unavailability of SCXRD result.

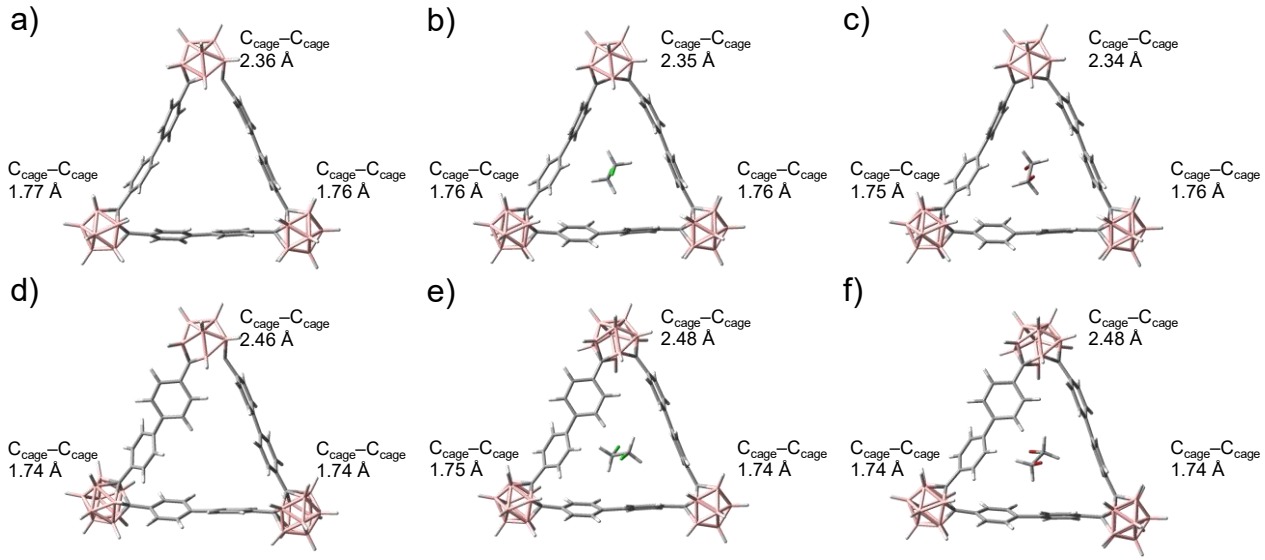


Figure S23. Optimized geometries of S_1 ICT (a–c) and dark states (d–f) of **CB3Ph6** in QM/MM modelling of **CB3Ph6**α (a,d), **DCE@CB3Ph6** (b,e) and **DBE@CB3Ph6** (c,f). Only QM-treated one molecule (accompanied with a guest molecule if existed) was shown for clarity. B3LYP/6-31+G(d,p) level was used. (colors: boron, pink; carbon, gray; hydrogen, white)

Table S5. Summary of relative energy of dark states[a]

Condition	Relative energy of dark states to ICT states / eV [b]
CB3Ph6α	0.19
DCE@CB3Ph6	0.38
DBE@CB3Ph6	0.44

[a] Calculated by QM/MM method. [b] Electronic energy was used for calculation.

NMR and MS Spectra

Charts S5–S7 were measured at least 30 min after the solid-vapor adsorption experiments.

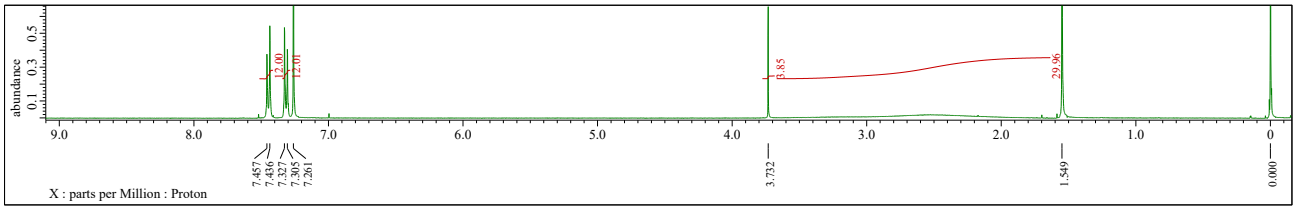


Chart S1. ^{1}H NMR spectra of **DCE@CB3Ph6** in $CDCl_3$.

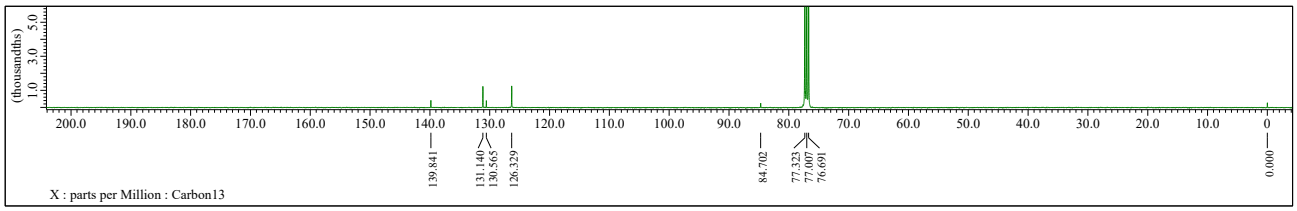


Chart S2. $^{13}C\{^{1}H\}$ NMR spectra of **CB3Ph6** in $CDCl_3$.

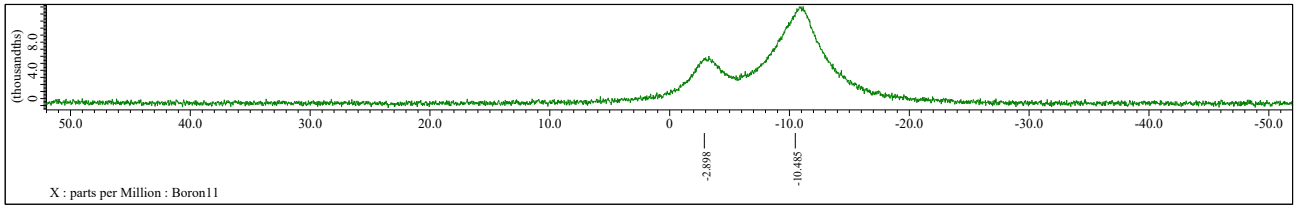


Chart S3. $^{11}B\{^{1}H\}$ NMR spectra of **CB3Ph6** in $CDCl_3$.

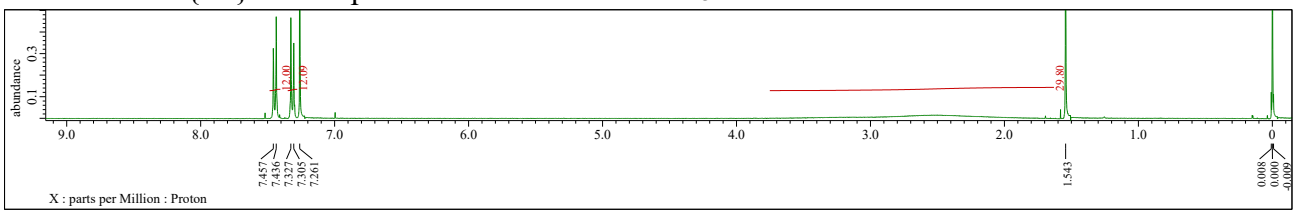


Chart S4. ^{1}H NMR spectra of **CB3Ph6**α in $CDCl_3$.

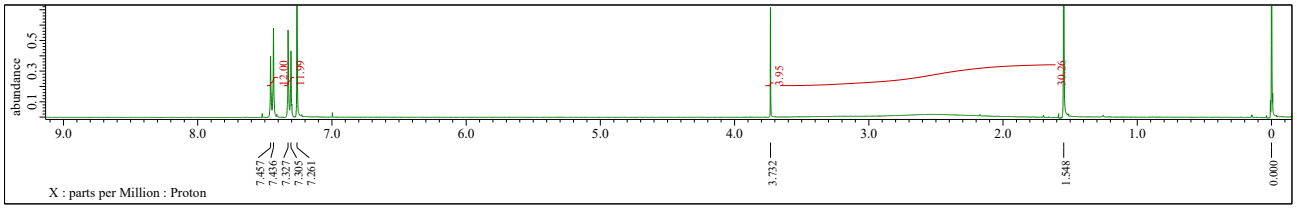


Chart S5. ^{1}H NMR spectra of **DBE@CB3Ph6** in $CDCl_3$.

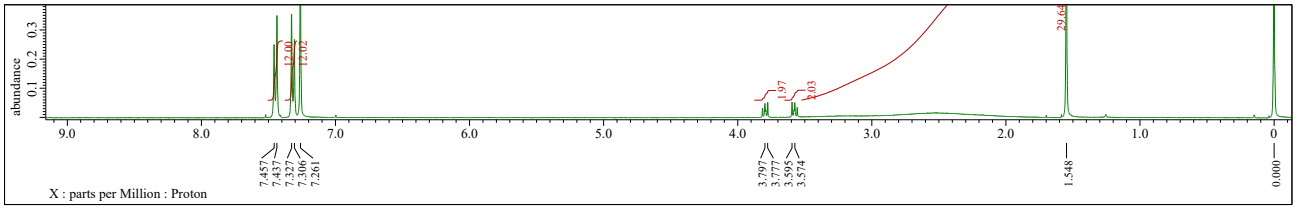


Chart S6. ^{1}H NMR spectra of **BCE@CB3Ph6** in $CDCl_3$.

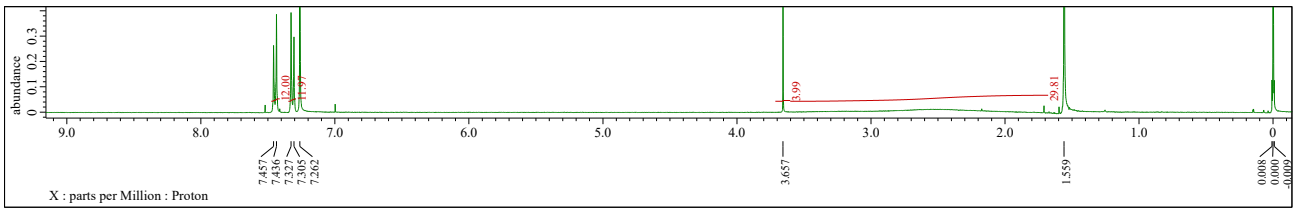


Chart S7. ^{1}H NMR spectra of **CB3Ph6**α in $CDCl_3$ after exposed to DCE vapor (**DCE-fumed**).

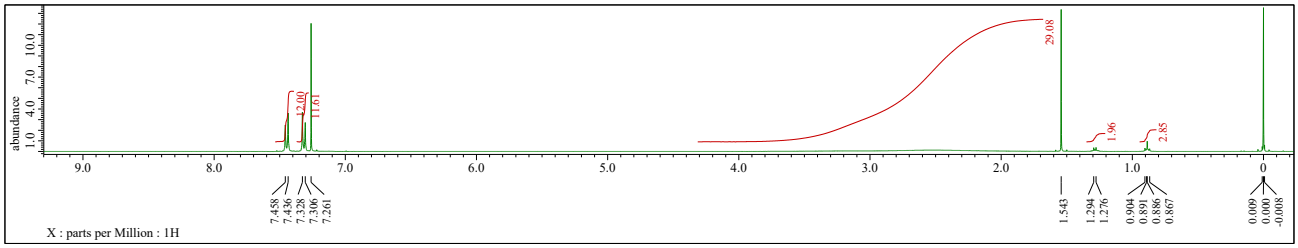


Chart S8. ^{1}H NMR spectra of **CB3Ph6**α in $CDCl_3$ measured within 30 min after the solid-gas adsorption experiment with C_4H_{10}. C_4H_{10}/**CB3Ph6** molar ratio was calculated as 0.49.

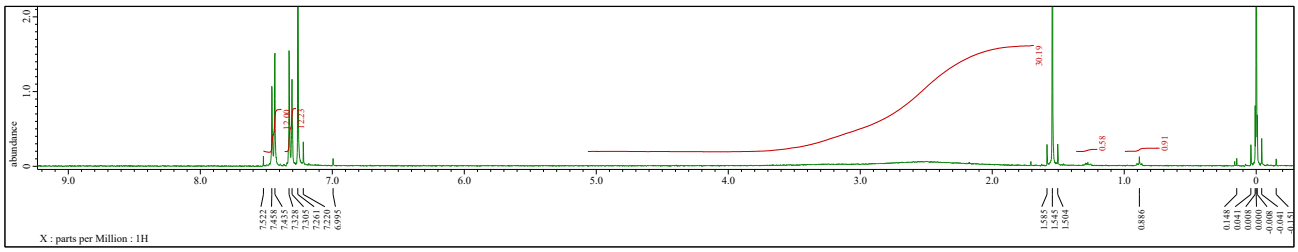


Chart S9. ^{1}H NMR spectra of **CB3Ph6**α in $CDCl_3$ measured 2 days after the solid-gas adsorption experiment with C_4H_{10}. C_4H_{10}/**CB3Ph6** molar ratio was calculated as 0.13.

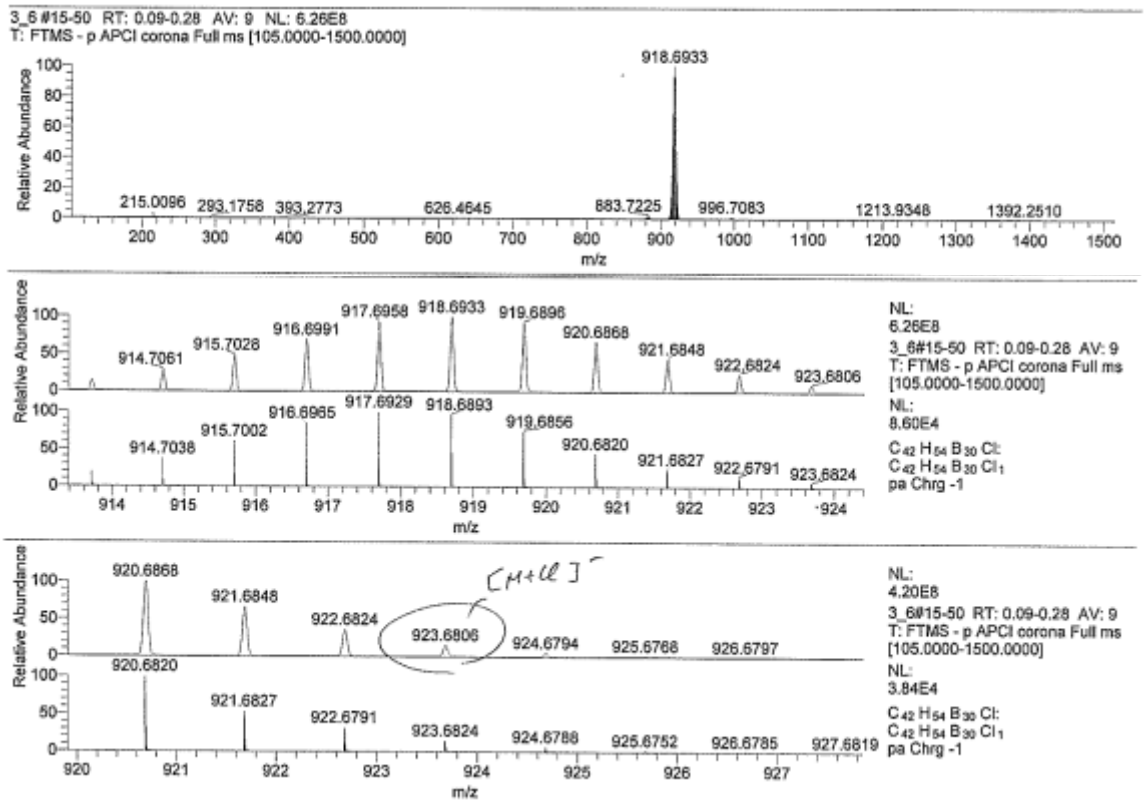


Chart S10. HRMS (APCI) spectrum of **CB3Ph6**.

Cartesian Coordinates of Optimized Geometries

Table S6. Optimized geometry of isolated **CB3Ph6** at the S_0 state

Center Number	Atomic Number	Coordinates (Angstroms)			Center Number	Atomic Number	Coordinates (Angstroms)		
		x	y	z			x	y	z
1	6	1.127448	-5.19476	-0.04387	64	1	-7.588513	2.545662	1.351184
2	6	3.921718	-3.5988	0.046533	65	1	-9.18376	0.173144	2.477635
3	6	3.942841	3.575649	-0.04636	66	1	-9.184721	-0.118866	-2.477574
4	6	-5.07728	-1.59336	0.053969	67	1	-6.116702	0.165633	2.336586
5	6	1.158023	5.188086	0.043816	68	1	-7.57581	2.381613	-1.636698
6	5	3.381648	5.952468	-1.41423	69	1	-6.11764	-0.129624	-2.336624
7	5	2.602883	7.430306	-0.80676	70	1	-10.170455	-1.506095	0.0844
8	5	3.83701	8.376206	0.050237	71	1	-10.161299	1.566221	-0.084294
9	5	5.373805	7.486859	-0.04075	72	6	3.571331	-2.857392	1.184203
10	5	5.097493	5.988658	-0.9612	73	6	3.58374	-1.464324	1.16341
11	5	5.167262	5.943325	0.811884	74	6	3.956149	-0.753731	0.010675
12	5	4.38414	7.405785	1.446432	75	6	4.322487	-1.500611	-1.121802
13	5	2.674166	7.387653	0.96628	76	6	4.302775	-2.892453	-1.105737
14	6	2.454418	5.958256	0.047097	77	6	3.58921	2.836305	-1.184374
15	5	3.496983	5.880687	1.416603	78	6	3.593426	1.443189	-1.163577
16	6	3.966122	5.083376	-0.0461	79	6	3.960532	0.730425	-0.01048
17	5	4.262095	7.481669	-1.43878	80	6	4.330206	1.475142	1.122337
18	1	1.639536	7.826537	-1.3656	81	6	4.318702	2.867077	1.10625
19	1	1.755677	7.738745	1.623387	82	6	0.661979	-4.519466	-1.181485
20	1	5.990076	5.304306	1.370365	83	6	-0.545889	-3.825452	-1.158436
21	1	4.720379	7.871939	2.483158	84	6	-1.343676	-3.784765	-0.003301
22	1	4.500375	8.008142	-2.47375	85	6	-0.880959	-4.475263	1.129595
23	1	3.187892	5.216101	2.337593	86	6	0.329303	-5.162959	1.111019
24	1	5.860584	5.368998	-1.61878	87	6	-4.256008	-1.651573	1.189226
25	1	2.961216	5.355781	-2.33762	88	6	-3.054364	-2.356667	1.168782
26	1	3.772074	9.559529	0.080611	89	6	-2.62767	-3.040407	0.01863
27	1	6.432261	8.020091	-0.06796	90	6	-3.461569	-2.993095	-1.111331
28	5	3.462368	-5.90103	-1.41657	91	6	-4.658603	-2.282863	-1.09546
29	5	5.132208	-5.97366	-0.81174	92	6	0.35966	5.161099	-1.111048
30	5	5.329545	-7.51844	0.040764	93	6	-0.854605	4.480493	-1.129661
31	5	3.787515	-8.39864	-0.05039	94	6	-1.321297	3.792565	0.003167
32	5	2.630606	-7.40315	-0.96642	95	6	-0.52322	3.828409	1.158262
33	5	2.55898	-7.44552	0.806631	96	6	0.688677	4.51536	1.181352
34	5	4.217815	-7.50676	1.438717	97	6	-2.609637	3.055759	-0.018758
35	5	5.062086	-6.0187	0.961323	98	6	-3.040397	2.374575	-1.168912
36	6	3.936133	-5.10664	0.04623	99	6	-4.246168	1.676555	-1.189308
37	5	3.346469	-5.97237	1.41427	100	6	-5.067711	1.623153	-0.054015
38	6	2.419291	-5.97255	-0.04713	101	6	-4.644933	2.310145	1.095416
39	5	4.340463	-7.43138	-1.44648	102	6	-3.443742	3.013319	1.111244
40	1	5.958863	-5.33953	-1.37011	103	1	3.277688	-3.362825	2.095209
41	1	5.828806	-5.40364	1.618992	104	1	3.275947	-0.925129	2.053825
42	1	1.593265	-7.83607	1.365388	105	1	4.652732	-0.990867	-2.021491
43	1	4.452904	-8.03473	2.473664	106	1	4.6053	-3.430549	-1.996173
44	1	4.674004	-7.89944	-2.48322	107	1	3.299449	3.343457	-2.095669
45	1	2.929576	-5.3733	2.337716	108	1	3.283349	0.905809	-2.054297
46	1	1.710074	-7.74873	-1.62359	109	1	4.656617	0.963467	2.022328
47	1	3.157302	-5.23449	-2.33749	110	1	4.623599	3.403399	1.996947
48	1	6.38482	-8.05794	0.067985	111	1	1.243525	-4.524143	-2.094439
49	1	3.715566	-9.58156	-0.08085	112	1	-0.858534	-3.289601	-2.049198
50	5	-6.84635	-0.05678	-1.41506	113	1	-1.484873	-4.499826	2.031293
51	5	-7.74042	-1.46449	-0.79939	114	1	0.643052	-5.694604	2.001419
52	5	-9.17684	-0.8603	0.051441	115	1	-4.545114	-1.139215	2.097849
53	5	-9.17155	0.914511	-0.05137	116	1	-2.430458	-2.353293	2.057093
54	5	-7.73396	1.415514	-0.97313	117	1	-3.186951	-3.538927	-2.008537
55	5	-7.73153	1.510121	0.7994	118	1	-5.278957	-2.282755	-1.983746
56	5	-8.61043	0.10696	1.44224	119	1	0.67648	5.690999	-2.001401
57	5	-7.74223	-1.36985	0.973152	120	1	-1.458406	4.508698	-2.031327
58	6	-6.39164	-0.85416	0.052341	121	1	-0.83894	3.294252	2.048958
59	5	-6.84584	0.097114	1.415033	122	1	1.270293	4.516498	2.094271
60	6	-6.38644	0.891773	-0.05237	123	1	-2.416565	2.367566	-2.057254
61	5	-8.61097	-0.0561	-1.4422	124	1	-4.538349	1.165914	-2.097915
62	1	-7.6036	-2.50087	-1.35117	125	1	-5.265236	2.313674	1.983729
63	1	-7.58982	-2.33688	1.636717	126	1	-3.165867	3.557502	2.00845

Table S7. Optimized geometry of isolated **CB3Ph6** at the S_1 ICT state

Center Number	Atomic Number	Coordinates (Angstroms)			Center Number	Atomic Number	Coordinates (Angstroms)		
		x	y	z			x	y	z
1	6	-0.95501	5.44242	-0.00898	64	1	-6.31728	-4.75961	-1.64296
2	6	2.913071	4.714745	0.029217	65	1	-8.73552	-3.02791	-2.47673
3	6	5.036381	-2.1344	-0.05113	66	1	-8.63265	-3.32487	2.477553
4	6	-5.475	-0.14883	0.072209	67	1	-5.88985	-1.88094	-2.32467
5	6	2.781419	-4.4714	0.016651	68	1	-6.27494	-4.93293	1.346137
6	5	5.214825	-4.47527	1.404231	69	1	-5.78422	-2.18296	2.344022
7	5	4.849918	-6.15103	0.944491	70	1	-10.1688	-2.11741	0.087893
8	5	6.252659	-6.77065	0.037775	71	1	-9.02296	-4.96729	-0.09339
9	5	7.48131	-5.48794	-0.0351	72	6	3.311631	4.086206	-1.18012
10	5	6.845779	-4.06898	0.820915	73	6	3.757166	2.779784	-1.19686
11	5	6.807231	-4.12263	-0.95654	74	6	3.86516	2.017154	-0.00022
12	5	6.422528	-5.78615	-1.44563	75	6	3.526842	2.673672	1.216436
13	5	4.809324	-6.20433	-0.83132	76	6	3.065834	3.975805	1.229777
14	6	4.241677	-4.84225	0.025236	77	6	5.156441	-1.35818	1.121666
15	5	5.148863	-4.56348	-1.42386	78	6	4.790341	-0.02431	1.139786
16	6	5.46274	-3.5748	-0.04921	79	6	4.283936	0.622641	-0.01994
17	5	6.49287	-5.69421	1.442401	80	6	4.190099	-0.16419	-1.19966
18	1	4.062126	-6.74634	1.59457	81	6	4.554478	-1.50003	-1.21315
19	1	4.0013	-6.8495	-1.40326	82	6	-1.51017	4.962618	1.20496
20	1	7.37037	-3.31058	-1.60631	83	6	-2.40994	3.910878	1.219348
21	1	6.808198	-6.21868	-2.47903	84	6	-2.81759	3.266991	0.025817
22	1	6.934905	-6.05331	2.481366	85	6	-2.29047	3.770491	-1.18763
23	1	4.589137	-4.09902	-2.34935	86	6	-1.39048	4.822805	-1.20724
24	1	7.447833	-3.22561	1.390241	87	6	-5.36684	0.674742	-1.06393
25	1	4.722818	-3.92672	2.322215	88	6	-4.52464	1.778064	-1.07575
26	1	6.520637	-7.92453	0.064913	89	6	-3.73411	2.117763	0.045476
27	1	8.64643	-5.70284	-0.05371	90	6	-3.85819	1.290265	1.183907
28	5	1.265834	6.592963	1.247951	91	6	-4.70798	0.190912	1.199381
29	5	2.932192	7.322274	0.924446	92	6	2.122367	-4.01906	1.169962
30	5	2.613761	8.813245	-0.00185	93	6	0.758724	-3.7348	1.150863
31	5	0.883667	9.138832	-0.03336	94	6	-0.00789	-3.90216	-0.0148
32	5	0.000454	7.872632	0.877415	95	6	0.656015	-4.35934	-1.16637
33	5	0.02875	7.850831	-0.94606	96	6	2.020489	-4.63508	-1.15274
34	5	1.65096	8.345471	-1.44728	97	6	-1.46683	-3.62918	-0.02456
35	5	2.958519	7.30252	-0.87869	98	6	-2.2632	-3.90588	1.099847
36	6	2.348832	6.078995	0.025444	99	6	-3.634	-3.6653	1.089908
37	5	1.305597	6.564435	-1.24368	100	6	-4.27072	-3.14394	-0.04801
38	6	0.028448	6.517573	-0.01746	101	6	-3.48009	-2.8687	-1.1734
39	5	1.604093	8.375677	1.42356	102	6	-2.10632	-3.10249	-1.15879
40	1	3.858819	7.091112	1.630206	103	1	3.251381	4.643753	-2.10717
41	1	3.908049	7.059261	-1.54932	104	1	4.056424	2.345388	-2.14426
42	1	-0.9048	7.996523	-1.66426	105	1	3.584198	2.135302	2.155764
43	1	1.765392	8.886662	-2.49803	106	1	2.790798	4.436931	2.17054
44	1	1.682115	8.942262	2.464172	107	1	5.555575	-1.80489	2.0239
45	1	1.190908	5.836742	-2.17388	108	1	4.927593	0.53759	2.056097
46	1	-0.95563	8.036661	1.561337	109	1	3.792016	0.27127	-2.10841
47	1	1.105675	5.890789	2.19077	110	1	4.45751	-2.05945	-2.13435
48	1	3.410728	9.693707	0.000205	111	1	-1.22932	5.437193	2.138491
49	1	0.455282	10.24652	-0.0525	112	1	-2.82838	3.598657	2.170707
50	5	-6.48717	-2.38227	1.420888	113	1	-2.5637	3.305431	-2.12918
51	5	-7.86429	-1.34954	0.984934	114	1	-0.99732	5.170121	-2.15583
52	5	-9.00683	-2.34966	0.055501	115	1	-5.96252	0.462523	-1.9438
53	5	-8.34508	-3.99557	-0.05481	116	1	-4.50274	2.402702	-1.96198
54	5	-6.78837	-4.02044	0.797526	117	1	-3.25937	1.491936	2.065266
55	5	-6.82248	-3.92459	-0.97481	118	1	-4.76451	-0.41111	2.097289
56	5	-8.1807	-2.87928	-1.4399	119	1	2.668786	-3.88842	2.095475
57	5	-7.89563	-1.25222	-0.78805	120	1	0.288985	-3.36504	2.056797
58	6	-6.41802	-1.32052	0.065379	121	1	0.094882	-4.53601	-2.07849
59	5	-6.54125	-2.22474	-1.40622	122	1	2.487473	-5.00793	-2.05664
60	6	-5.76582	-2.94618	-0.04754	123	1	-1.8152	-4.34534	1.9855
61	5	-8.12392	-3.04519	1.444176	124	1	-4.21443	-3.90887	1.97165
62	1	-8.08196	-0.39913	1.654018	125	1	-3.93124	-2.46624	-2.07127
63	1	-8.15433	-0.23744	-1.33575	126	1	-1.52454	-2.85287	-2.04064

Table S8. Optimized geometry of isolated **CB3Ph6** at the S_1 dark state

Center Number	Atomic Number	Coordinates (Angstroms)			Center Number	Atomic Number	Coordinates (Angstroms)		
		x	y	z			x	y	z
1	6	2.260693	4.989321	0.022433	64	1	4.931117	-6.09309	1.668617
2	6	-1.801709	5.349635	-0.076842	65	1	7.736509	-5.06145	2.468495
3	6	-5.464123	-0.836664	0.054806	66	1	7.517399	-5.39034	-2.48168
4	6	5.322193	-1.465483	-0.123096	67	1	5.298933	-3.17296	2.307186
5	6	-3.79039	-3.615197	0.017199	68	1	4.823452	-6.29518	-1.30964
6	5	-6.161063	-3.093872	-1.380603	69	1	5.085953	-3.50757	-2.357
7	5	-6.168219	-4.80689	-0.909128	70	1	9.337868	-4.60182	-0.11572
8	5	-7.670283	-5.1054	-0.002929	71	1	7.47239	-7.04067	0.116398
9	5	-8.592552	-3.587706	0.060453	72	6	-2.37162	4.858499	1.119091
10	5	-7.66378	-2.342948	-0.798922	73	6	-3.14191	3.70271	1.13205
11	5	-7.640434	-2.392715	0.974733	74	6	-3.38382	2.965918	-0.04429
12	5	-7.62776	-4.097138	1.473645	75	6	-2.86265	3.484156	-1.24557
13	5	-6.142804	-4.855536	0.865229	76	6	-2.09664	4.646215	-1.26507
14	6	-5.29906	-3.6463	0.003734	77	6	-5.51322	-0.01351	-1.08261
15	5	-6.120907	-3.176015	1.450207	78	6	-4.86465	1.217684	-1.10971
16	6	-6.2054	-2.147931	0.06921	79	6	-4.11878	1.679258	-0.00947
17	5	-7.67115	-4.008732	-1.413707	80	6	-4.07684	0.849618	1.125991
18	1	-5.523718	-5.564238	-1.54975	81	6	-4.74077	-0.3738	1.163452
19	1	-5.491908	-5.657813	1.44009	82	6	3.668414	4.863315	0.220898
20	1	-8.019854	-1.476158	1.618157	83	6	4.280528	3.630395	0.206272
21	1	-8.098068	-4.432255	2.508893	84	6	3.535633	2.444075	-0.06984
22	1	-8.180364	-4.269982	-2.451835	85	6	2.133335	2.571344	-0.29053
23	1	-5.475634	-2.843555	2.376974	86	6	1.513493	3.794445	-0.21476
24	1	-8.080339	-1.39874	-1.374196	87	6	5.819248	-0.45519	0.723632
25	1	-5.560812	-2.666899	-2.299322	88	6	5.277659	0.821133	0.710862
26	1	-8.179622	-6.17581	-0.024321	89	6	4.168678	1.134117	-0.11099
27	1	-9.777267	-3.547762	0.075596	90	6	3.674676	0.113739	-0.95846
28	5	0.442278	6.640465	-1.170324	91	6	4.254916	-1.14483	-0.98233
29	5	-0.939555	7.861011	-0.937562	92	6	-3.04194	-3.30812	-1.12822
30	5	-0.208738	9.167771	0.034386	93	6	-1.64939	-3.35807	-1.10896
31	5	1.546371	9.018438	0.098684	94	6	-0.94705	-3.72337	0.051251
32	5	2.098036	7.595965	-0.795522	95	6	-1.69977	-4.02189	1.199221
33	5	2.023805	7.561959	0.981297	96	6	-3.09105	-3.96755	1.18276
34	5	0.5588	8.406409	1.475798	97	6	0.535181	-3.81899	0.056916
35	5	-1.009429	7.811235	0.872898	98	6	1.233193	-4.2872	-1.07017
36	6	-0.890489	6.497401	-0.058375	99	6	2.620694	-4.39544	-1.06834
37	5	0.368307	6.586559	1.176579	100	6	3.374555	-4.04351	0.063818
38	6	1.585777	6.279211	0.044543	101	6	2.683126	-3.5856	1.195103
39	5	0.670363	8.464861	-1.378283	102	6	1.293376	-3.47092	1.187673
40	1	-1.84625	7.976454	-1.694513	103	1	-2.19924	5.393451	2.046777
41	1	-1.97033	7.901069	1.563687	104	1	-3.57313	3.373879	2.07271
42	1	2.941637	7.416055	1.721029	105	1	-3.02584	2.952969	-2.17865
43	1	0.549921	8.908613	2.552366	106	1	-1.69783	5.00443	-2.20825
44	1	0.761012	9.012097	-2.428808	107	1	-6.08048	-0.32434	-1.95206
45	1	0.278985	5.816494	2.075946	108	1	-4.95975	1.836863	-1.9959
46	1	3.070842	7.474452	-1.466163	109	1	-3.49793	1.151742	1.992529
47	1	0.449327	5.918524	-2.113246	110	1	-4.68039	-0.97124	2.064258
48	1	-0.719125	10.240682	0.042459	111	1	4.251597	5.760536	0.390915
49	1	2.222896	9.994296	0.143281	112	1	5.352959	3.563212	0.355959
50	5	5.709788	-3.898098	-1.437353	113	1	1.537542	1.682888	-0.46757
51	5	7.316211	-3.261014	-1.016082	114	1	0.441249	3.864404	-0.34647
52	5	8.15672	-4.518389	-0.07618	115	1	6.634864	-0.6721	1.400553
53	5	7.079665	-5.924193	0.064131	116	1	5.67632	1.567642	1.389177
54	5	5.5677	-5.544125	-0.783288	117	1	2.853766	0.324778	-1.6346
55	5	5.638554	-5.43269	0.990066	118	1	3.864665	-1.88436	-1.66741
56	5	7.231221	-4.787263	1.432734	119	1	-3.54226	-3.02951	-2.04682
57	5	7.387256	-3.158361	0.754284	120	1	-1.10518	-3.09603	-2.01114
58	6	5.93249	-2.845356	-0.09061	121	1	-1.19845	-4.3379	2.108807
59	5	5.826051	-3.713336	1.402674	122	1	-3.63507	-4.22917	2.08231
60	6	4.87346	-4.222631	0.049427	123	1	0.684074	-4.60405	-1.95109
61	5	7.109377	-4.972196	-1.451168	124	1	3.115325	-4.78023	-1.95241
62	1	7.769543	-2.408081	-1.698365	125	1	3.223917	-3.31188	2.092626
63	1	7.929865	-2.257512	1.29061	126	1	0.795402	-3.09096	2.07424

Table S9. Optimized geometry of QM/MM-treated **CB3Ph6** in **CB3Ph6**α at the S_1 ICT state

Center Number	Atomic Number	Coordinates (Angstroms)			Center Number	Atomic Number	Coordinates (Angstroms)		
		x	y	z			x	y	z
883	6	5.053161	0.618658	2.02942	946	6	5.06468	-0.98404	2.748257
884	6	3.748611	1.305124	1.735841	947	6	3.760783	-1.66605	3.065634
885	6	3.095	1.132445	0.504861	948	6	3.232663	-1.60359	4.362764
886	1	3.495333	0.430355	-0.212076	949	1	3.754803	-1.03778	5.121151
887	6	1.960359	1.862793	0.176587	950	6	2.081551	-2.30217	4.70817
888	1	1.501423	1.681772	-0.788422	951	1	1.748013	-2.25287	5.738584
889	6	1.413091	2.826318	1.056883	952	6	1.391132	-3.09034	3.768857
890	6	2.064417	2.969423	2.306912	953	6	1.923055	-3.1435	2.46696
891	1	1.714333	3.702643	3.02409	954	1	1.42716	-3.72281	1.695635
892	6	3.196015	2.235043	2.634252	955	6	3.085317	-2.45633	2.124385
893	1	3.672354	2.409491	3.589573	956	1	3.466654	-2.54396	1.115164
894	6	0.247355	3.647345	0.685301	957	6	0.150516	-3.82481	4.13592
895	6	-0.244613	3.697763	-0.645381	958	6	-0.58459	-3.48346	5.285213
896	1	0.289504	3.191758	-1.442327	959	1	-0.23761	-2.6939	5.941825
897	6	-1.402294	4.383125	-0.973766	960	6	-1.78759	-4.10881	5.598173
898	1	-1.751568	4.378258	-2.000914	961	1	-2.30834	-3.80777	6.49826
899	6	-2.155177	5.077213	0.010167	962	6	-2.33325	-5.0914	4.758669
900	6	-1.597639	5.128358	1.315592	963	6	-1.5765	-5.48266	3.641852
901	1	-2.109645	5.687157	2.089071	964	1	-1.93534	-6.27182	2.992871
902	6	-0.446677	4.432612	1.639711	965	6	-0.35973	-4.87348	3.346556
903	1	-0.10315	4.475162	2.667455	966	1	0.193132	-5.22809	2.483558
904	6	-3.466826	5.634297	-0.27671	967	6	-3.67914	-5.70933	5.032358
905	6	-5.371434	4.320353	0.162612	968	6	-5.13143	-4.77684	4.622491
906	6	-5.267985	2.988162	0.791066	969	6	-5.0121	-3.41289	4.000377
907	6	-4.845412	1.83784	0.079656	970	6	-4.7592	-2.24604	4.747682
908	1	-4.602292	1.934094	-0.970212	971	1	-4.58768	-2.31904	5.813023
909	6	-4.740095	0.609137	0.702954	972	6	-4.73904	-0.99965	4.139845
910	1	-4.411788	-0.244812	0.123537	973	1	-4.5283	-0.12786	4.744824
911	6	-4.998121	0.455853	2.09495	974	6	-4.95438	-0.84587	2.743581
912	6	-5.368002	1.623378	2.811986	975	6	-5.18387	-2.03084	2.001073
913	1	-5.549406	1.573025	3.874649	976	1	-5.38032	-1.9735	0.939615
914	6	-5.546824	2.829847	2.173384	977	6	-5.22617	-3.26496	2.616906
915	1	-5.899243	3.68085	2.734484	978	1	-5.45537	-4.13289	2.02575
916	5	6.40348	0.77385	0.981773	979	5	6.41311	-1.13	3.794557
917	1	6.251435	1.435681	0.013067	980	1	6.268703	-1.79503	4.762548
918	5	6.399894	1.502167	2.603288	981	5	6.412684	-1.85983	2.174298
919	1	6.252403	2.667823	2.731842	982	1	6.269197	-3.02638	2.046768
920	5	5.512186	0.400689	3.681654	983	5	5.515514	-0.76259	1.097142
921	1	4.776921	0.776491	4.521799	984	1	4.796098	-1.15128	0.24994
922	5	7.834839	0.634509	2.028939	985	5	7.842402	-0.98156	2.749386
923	1	8.827347	1.229995	1.802694	986	1	8.839746	-1.56812	2.982587
924	5	7.275412	0.418821	3.708984	987	5	7.279904	-0.76859	1.068859
925	1	7.848916	0.849433	4.652567	988	1	7.854021	-1.19545	0.124065
926	5	-4.617984	4.684738	-1.305084	989	5	-4.68624	-5.03051	6.265883
927	1	-4.145143	3.807674	-1.948628	990	1	-4.28606	-4.1237	6.897938
928	5	-6.444766	4.759322	-1.012874	991	5	-6.37626	-5.14838	5.730272
929	1	-7.17188	3.927557	-1.439124	992	1	-7.10513	-4.26767	6.021036
930	5	-6.464735	5.434906	0.64902	993	5	-6.35272	-5.83975	4.093397
931	1	-7.205254	5.095899	1.506946	994	1	-7.07064	-5.42797	3.252349
932	5	-4.683343	5.652948	1.013682	995	5	-4.65315	-6.13396	3.66171
933	1	-4.301723	5.45814	2.118664	996	1	-4.20417	-5.92623	2.592697
934	5	-4.065984	7.101934	0.072557	997	5	-3.99789	-7.36449	4.761716
935	1	-3.306919	7.887847	0.534464	998	1	-3.10068	-8.02692	4.37479
936	5	-4.014556	6.37905	-1.607718	999	5	-4.01215	-6.66812	6.400933
937	1	-3.209638	6.583211	-2.452216	1000	1	-3.11531	-6.82452	7.15397
938	5	-5.677406	5.964482	-2.047311	1001	5	-5.70474	-6.35695	6.843519
939	1	-6.000959	6.026511	-3.183731	1002	1	-6.07306	-6.40586	7.965612
940	5	-5.761626	7.055191	0.596208	1003	5	-5.67609	-7.47358	4.186525
941	1	-6.126224	7.867985	1.37718	1004	1	-6.0115	-8.30875	3.421471
942	5	-5.370554	7.451872	-1.102253	1005	5	-5.28923	-7.80689	5.896108
943	1	-5.470678	8.541584	-1.553335	1006	1	-5.35158	-8.89594	6.347972
944	5	-6.79911	6.484454	-0.748534	1007	5	-6.73926	-6.87137	5.4878
945	1	-7.889664	6.901815	-0.964559	1008	1	-7.83487	-7.28478	5.665222

Table S10. Optimized geometry of QM/MM-treated **CB3Ph6** in **CB3Ph6**α at the S_1 dark state

Center Number	Atomic Number	Coordinates (Angstroms)			Center Number	Atomic Number	Coordinates (Angstroms)		
		x	y	z			x	y	z
883	6	5.129726	0.586207	2.059985	946	6	5.129967	-1.00605	2.768002
884	6	3.826841	1.268849	1.753891	947	6	3.81866	-1.68776	3.05553
885	6	3.250018	1.16737	0.480243	948	6	3.14191	-1.48388	4.265306
886	1	3.717897	0.541161	-0.26598	949	1	3.534668	-0.77908	4.983969
887	6	2.121655	1.902418	0.135334	950	6	1.974571	-2.18145	4.562986
888	1	1.751709	1.810775	-0.87909	951	1	1.473577	-1.97627	5.503501
889	6	1.506589	2.785447	1.0453	952	6	1.440081	-3.12334	3.667706
890	6	2.07246	2.848384	2.336114	953	6	2.123921	-3.32553	2.455858
891	1	1.643941	3.497033	3.09113	954	1	1.774067	-4.07085	1.749249
892	6	3.205552	2.119174	2.679825	955	6	3.283806	-2.62015	2.155313
893	1	3.618562	2.234538	3.67369	956	1	3.786855	-2.8135	1.219085
894	6	0.353318	3.635842	0.657691	957	6	0.192978	-3.86523	3.980923
895	6	-0.29767	3.496948	-0.58734	958	6	-0.21483	-4.11231	5.304953
896	1	0.059803	2.778068	-1.31629	959	1	0.422929	-3.827	6.134322
897	6	-1.42743	4.235452	-0.91074	960	6	-1.4363	-4.71922	5.586849
898	1	-1.91585	4.066062	-1.86447	961	1	-1.71492	-4.88392	6.621996
899	6	-1.98827	5.163369	-0.0011	962	6	-2.3022	-5.11078	4.553638
900	6	-1.2674	5.389595	1.192294	963	6	-1.86123	-4.94585	3.231681
901	1	-1.62397	6.130706	1.894093	964	1	-2.47469	-5.27294	2.402609
902	6	-0.14143	4.644413	1.512027	965	6	-0.64536	-4.33013	2.953815
903	1	0.354592	4.860709	2.451409	966	1	-0.37146	-4.17638	1.915437
904	6	-3.32079	5.713279	-0.21583	967	6	-3.66336	-5.67781	4.864769
905	6	-5.23573	4.604192	0.860154	968	6	-5.05515	-4.64682	4.684821
906	6	-5.07533	3.445211	1.729575	969	6	-4.86438	-3.22767	4.192691
907	6	-6.21285	2.738525	2.210972	970	6	-4.05185	-2.29604	4.865502
908	1	-7.1952	3.173587	2.071223	971	1	-3.49961	-2.59391	5.746375
909	6	-6.06791	1.479647	2.739533	972	6	-3.94719	-0.97792	4.427539
910	1	-6.94051	0.896527	2.993911	973	1	-3.31517	-0.2851	4.973726
911	6	-4.7882	0.892579	2.946198	974	6	-4.7243	-0.51722	3.346093
912	6	-3.64269	1.697512	2.693393	975	6	-5.50974	-1.46334	2.649846
913	1	-2.65174	1.302946	2.893556	976	1	-6.08464	-1.14844	1.785721
914	6	-3.78263	2.92031	2.070973	977	6	-5.54668	-2.79511	3.040064
915	1	-2.90082	3.479698	1.787878	978	1	-6.14449	-3.49284	2.467063
916	5	6.479885	0.746076	1.012351	979	5	6.477464	-1.1754	3.814849
917	1	6.330887	1.418498	0.050661	980	1	6.323496	-1.84637	4.777544
918	5	6.478185	1.463619	2.637748	981	5	6.470807	-1.89167	2.189081
919	1	6.333391	2.628616	2.774005	982	1	6.321403	-3.0568	2.055375
920	5	5.589435	0.362042	3.711897	983	5	5.584858	-0.78623	1.114964
921	1	4.869143	0.744452	4.56098	984	1	4.851336	-1.16621	0.275821
922	5	7.9085	0.592347	2.057444	985	5	7.904783	-1.02819	2.765633
923	1	8.904741	1.182737	1.835442	986	1	8.89837	-1.6243	2.980503
924	5	7.350434	0.368387	3.73563	987	5	7.34494	-0.80135	1.088188
925	1	7.923574	0.791311	4.682357	988	1	7.915822	-1.22855	0.14193
926	5	-4.57482	4.558267	-0.70852	989	5	-4.51036	-5.07666	6.261826
927	1	-4.19565	3.502142	-1.0938	990	1	-3.98989	-4.2562	6.927135
928	5	-6.4282	4.742042	-0.2884	991	5	-6.24054	-5.05754	5.857799
929	1	-7.17892	3.833214	-0.40299	992	1	-6.90053	-4.17877	6.287378
930	5	-6.30776	5.826468	1.103676	993	5	-6.39189	-5.58919	4.173951
931	1	-6.95551	5.79844	2.091811	994	1	-7.17393	-5.08238	3.449928
932	5	-4.39008	6.020466	1.172161	995	5	-4.76333	-5.92972	3.559152
933	1	-3.89164	6.104739	2.245063	996	1	-4.41822	-5.62149	2.480262
934	5	-3.92984	7.212682	-0.14735	997	5	-4.08323	-7.29167	4.479637
935	1	-3.17532	8.094469	0.068502	998	1	-3.2367	-7.94439	3.977383
936	5	-4.04673	6.118883	-1.59687	999	5	-3.92622	-6.74681	6.166166
937	1	-3.37692	6.127006	-2.57673	1000	1	-2.97847	-7.0177	6.814019
938	5	-5.74913	5.579611	-1.68314	1001	5	-5.552	-6.40127	6.789415
939	1	-6.18527	5.303861	-2.74569	1002	1	-5.83767	-6.54013	7.926158
940	5	-5.55472	7.316341	0.555391	1003	5	-5.80773	-7.26131	4.050067
941	1	-5.84083	8.304984	1.133734	1004	1	-6.25066	-7.9942	3.236426
942	5	-5.35144	7.272324	-1.22877	1005	5	-5.29636	-7.77685	5.681806
943	1	-5.52854	8.205261	-1.93848	1006	1	-5.36977	-8.9012	6.043352
944	5	-6.73598	6.469029	-0.49109	1007	5	-6.72035	-6.73103	5.48964
945	1	-7.82352	6.87628	-0.73719	1008	1	-7.82341	-7.09577	5.720809

Table S11. Optimized geometry of QM/MM-treated **CB3Ph6** in **DCE@CB3Ph6** at the S_1 ICT state

Center Number	Atomic Number	Coordinates (Angstroms)			Center Number	Atomic Number	Coordinates (Angstroms)		
		x	y	z			x	y	z
883	6	5.362134	-1.75771	2.697985	950	6	2.091844	5.419565	4.735256
884	1	5.646819	-1.70587	3.73889	951	6	1.564558	5.435365	3.416529
885	6	5.20738	-4.48051	0.06107	952	1	2.116444	5.936906	2.632457
886	6	3.775095	-5.4642	-0.24229	953	6	0.405134	4.758234	3.099623
887	6	2.421932	-4.88186	0.099786	954	1	0.084789	4.750122	2.064072
888	6	2.000598	-4.71935	1.429775	955	6	-0.31754	4.023035	4.08326
889	1	2.629298	-5.0467	2.24717	956	6	0.137627	4.136286	5.428525
890	6	0.787805	-4.10455	1.734147	957	1	-0.42744	3.677573	6.230972
891	1	0.536709	-3.95838	2.780041	958	6	1.291106	4.823739	5.746726
892	6	-0.07067	-3.63084	0.72655	959	1	1.619078	4.874827	6.778645
893	6	0.317647	-3.87228	-0.60487	960	6	-1.45626	3.187978	3.72601
894	1	-0.33451	-3.58455	-1.42252	961	6	-1.97463	2.206208	4.616472
895	6	1.537151	-4.47454	-0.91267	962	1	-1.49728	2.033825	5.573348
896	1	1.799475	-4.62223	-1.95445	963	6	-3.07891	1.440154	4.28492
897	6	-1.30769	-2.87176	1.062804	964	1	-3.45183	0.714919	4.993721
898	6	-1.84051	-1.90993	0.183878	965	6	-3.73552	1.599376	3.048995
899	1	-1.34339	-1.69832	-0.75671	966	6	-3.2156	2.549436	2.146054
900	6	-2.99633	-1.19697	0.498025	967	1	-3.70042	2.702546	1.192367
901	1	-3.38059	-0.47916	-0.21251	968	6	-2.11074	3.315417	2.468172
902	6	-3.67286	-1.4028	1.70932	969	1	-1.7784	4.060212	1.755588
903	6	-3.13912	-2.35216	2.596159	970	6	-5.01377	0.873363	2.74533
904	1	-3.64148	-2.55807	3.531023	971	6	4.805454	0.85501	4.068014
905	6	-1.9861	-3.06675	2.282069	972	1	4.557019	-0.01756	4.659517
906	1	-1.63911	-3.81822	2.983951	973	5	4.473481	4.976872	6.069564
907	6	-4.98799	-0.72464	2.004669	974	1	3.97115	4.095305	6.685018
908	6	4.653039	-0.73864	0.638463	975	5	4.603489	5.993989	3.776525
909	1	4.329699	0.123029	0.068045	976	1	4.238209	5.827751	2.661807
910	5	4.667833	-4.73347	-1.54821	977	5	6.295374	5.018534	5.827273
911	1	4.157923	-3.84511	-2.13049	978	1	7.010304	4.185082	6.271699
912	5	4.845411	-5.87345	1.038978	979	5	6.367084	5.730997	4.158207
913	1	4.487189	-5.70519	2.144405	980	1	7.13624	5.429225	3.312401
914	5	6.395732	-4.80062	-1.12886	981	5	3.998831	7.442578	4.748252
915	1	7.078873	-3.89472	-1.45431	982	1	3.230077	8.224713	4.295737
916	5	6.491429	-5.49885	0.498973	983	5	3.902433	6.691019	6.391135
917	1	7.240687	-5.05921	1.295594	984	1	3.057918	6.876763	7.201578
918	5	4.162155	-7.11972	-0.0226	985	5	5.541599	6.230823	6.862602
919	1	3.303259	-7.80838	0.408785	986	1	5.851101	6.252944	8.003742
920	5	4.049624	-6.39346	-1.64167	987	5	5.692892	7.364235	4.239588
921	1	3.117216	-6.57493	-2.34204	988	1	6.109488	8.173989	3.48324
922	5	5.69749	-6.02304	-2.19818	989	5	6.687198	6.751975	5.595132
923	1	6.005219	-6.06357	-3.33723	990	1	7.786854	7.131979	5.83236
924	5	5.879674	-7.16519	0.438383	991	5	5.276248	7.745158	5.946656
925	1	6.291666	-7.99174	1.176432	992	1	5.398847	8.822134	6.423055
926	5	6.83463	-6.51081	-0.91959	993	5	-5.46597	0.666761	1.090691
927	1	7.933764	-6.88181	-1.16208	994	1	-4.74524	1.071551	0.251535
928	5	5.393674	-7.49371	-1.24371	995	5	-6.35892	0.999165	3.801734
929	1	5.463831	-8.57226	-1.7156	996	1	-6.20736	1.654111	4.775511
930	5	-5.44349	-0.52152	3.665326	997	5	-6.37169	1.745543	2.184743
931	1	-4.70495	-0.90433	4.499311	998	1	-6.23797	2.914335	2.069881
932	5	-6.34343	-0.87226	0.96135	999	5	-7.23273	0.661658	1.070357
933	1	-6.19168	-1.51933	-0.01683	1000	1	-7.81434	1.094104	0.133049
934	5	-6.32635	-1.61814	2.575215	1001	5	-7.7915	0.853357	2.758309
935	1	-6.17345	-2.78433	2.686205	1002	1	-8.79083	1.431333	3.007993
936	5	-7.20803	-0.55622	3.698443	1003	6	5.000622	0.719532	2.67199
937	1	-7.77469	-1.00398	4.63776	1004	6	4.880726	2.087764	4.698201
938	5	-7.77271	-0.7539	2.01814	1005	1	4.697537	2.158531	5.763013
939	1	-8.76237	-1.35166	1.787759	1006	6	5.196334	3.263205	3.974226
940	6	4.988851	-0.58899	2.003697	1007	6	5.378561	3.123135	2.577668
941	6	4.686884	-1.97859	0.008173	1008	1	5.640068	3.992616	1.999161
942	1	4.410793	-2.04605	-1.0364	3459	17	1.215368	-0.54586	4.491843
943	6	5.077997	-3.13122	0.70838	3460	6	1.243476	-0.48683	2.671295
944	6	5.423424	-2.98467	2.061141	3461	1	2.109624	-1.06249	2.348701
945	1	5.782804	-3.83668	2.613068	3462	1	0.327943	-0.96473	2.327526
946	6	5.259035	1.902683	1.945574	3463	17	1.289801	1.017426	0.398851
947	1	5.394197	1.861628	0.87458	3464	6	1.324889	0.958239	2.219122
948	6	5.318524	4.573171	4.600283	3465	1	2.252585	1.433581	2.535185
949	6	3.445731	5.921424	5.026723	3466	1	0.469276	1.534244	2.565999

Table S12. Optimized geometry of QM/MM-treated **CB3Ph6** in **DCE@CB3Ph6** at the S_1 dark state

Center Number	Atomic Number	Coordinates (Angstroms)			Center Number	Atomic Number	Coordinates (Angstroms)		
		x	y	z			x	y	z
883	6	-5.50436	1.12402	2.087446	950	6	-1.89254	-5.60855	4.634112
884	1	-6.04808	0.823625	2.976941	951	6	-1.31237	-5.61956	3.348241
885	6	-5.10187	4.282052	0.000567	952	1	-1.79122	-6.17014	2.55055
886	6	-3.71957	5.338318	-0.17692	953	6	-0.19141	-4.85602	3.052082
887	6	-2.34464	4.807695	0.149861	954	1	0.167318	-4.8641	2.028731
888	6	-1.88388	4.725688	1.473523	955	6	0.437309	-4.05595	4.027024
889	1	-2.49233	5.091349	2.290668	956	6	-0.06499	-4.15101	5.341271
890	6	-0.65369	4.14523	1.772493	957	1	0.426631	-3.62551	6.151906
891	1	-0.36826	4.06706	2.816647	958	6	-1.19577	-4.89741	5.638415
892	6	0.180669	3.625122	0.766323	959	1	-1.57229	-4.90774	6.655566
893	6	-0.23893	3.814225	-0.56397	960	6	1.584021	-3.18048	3.685551
894	1	0.397603	3.504019	-1.38479	961	6	2.072136	-2.20288	4.57484
895	6	-1.47291	4.386097	-0.86709	962	1	1.590058	-2.04225	5.532318
896	1	-1.75711	4.496205	-1.90802	963	6	3.18328	-1.42491	4.262838
897	6	1.421493	2.872903	1.101278	964	1	3.547374	-0.71227	4.989979
898	6	1.971849	1.936017	0.208087	965	6	3.849197	-1.56962	3.037367
899	1	1.488578	1.736856	-0.74168	966	6	3.347214	-2.51419	2.131317
900	6	3.130318	1.22737	0.518826	967	1	3.833362	-2.6579	1.177054
901	1	3.530622	0.530981	-0.20424	968	6	2.249768	-3.30156	2.450017
902	6	3.789618	1.413359	1.741985	969	1	1.938033	-4.05052	1.732668
903	6	3.235707	2.33438	2.644101	970	6	5.133331	-0.84791	2.748108
904	1	3.720179	2.513834	3.592734	971	6	-3.68694	-2.08001	1.930664
905	6	2.08239	3.048266	2.331817	972	1	-2.71601	-1.73392	1.59809
906	1	1.723476	3.780713	3.047254	973	5	-4.40753	-4.92503	5.453069
907	6	5.10852	0.741955	2.035475	974	1	-3.9507	-3.89199	5.81622
908	6	-4.01143	0.611134	0.259243	975	5	-4.37605	-6.37074	3.584209
909	1	-3.38319	-0.08287	-0.28652	976	1	-3.95701	-6.46751	2.479598
910	5	-4.55017	4.711178	-1.57329	977	5	-6.29465	-5.0372	5.156024
911	1	-4.01044	3.897606	-2.23164	978	1	-7.01124	-4.10794	5.32627
912	5	-4.83629	5.575728	1.118456	979	5	-6.28517	-6.12246	3.75565
913	1	-4.49311	5.277575	2.201432	980	1	-6.98063	-6.07835	2.803427
914	5	-6.28512	4.667607	-1.18565	981	5	-3.89331	-7.61403	4.867038
915	1	-6.92746	3.777366	-1.61815	982	1	-3.18192	-8.52351	4.612827
916	5	-6.45647	5.205546	0.494519	983	5	-3.88804	-6.51316	6.31105
917	1	-7.23261	4.686552	1.216713	984	1	-3.17152	-6.54456	7.256829
918	5	-4.17347	6.945631	0.19538	985	5	-5.55677	-5.90774	6.49985
919	1	-3.34245	7.616313	0.700982	986	1	-5.90204	-5.61937	7.591262
920	5	-3.99594	6.390982	-1.48671	987	5	-5.55736	-7.63875	4.255602
921	1	-3.04705	6.66553	-2.13021	988	1	-5.92222	-8.60402	3.684241
922	5	-5.61273	6.016356	-2.11896	989	5	-6.64722	-6.75594	5.36631
923	1	-5.89567	6.146616	-3.25756	990	1	-7.73764	-7.12391	5.6575
924	5	-5.90059	6.888595	0.613351	991	5	-5.25423	-7.61498	6.022329
925	1	-6.36056	7.619959	1.419923	992	1	-5.4276	-8.54358	6.73878
926	5	-6.79564	6.3347	-0.83068	993	5	5.591856	-0.62039	1.094483
927	1	-7.90337	6.678594	-1.07175	994	1	4.873456	-1.01347	0.248265
928	5	-5.38677	7.402103	-1.01889	995	5	6.480462	-0.98966	3.800196
929	1	-5.47354	8.52229	-1.38946	996	1	6.332895	-1.66232	4.762003
930	5	5.563161	0.52945	3.691507	997	5	6.494615	-1.70871	2.17439
931	1	4.824119	0.899912	4.530253	998	1	6.366701	-2.87556	2.039135
932	5	6.461402	0.925351	0.991698	999	5	7.353904	-0.60631	1.0771
933	1	6.304653	1.591858	0.026651	1000	1	7.934892	-1.02302	0.132477
934	5	6.437719	1.644129	2.615194	1001	5	7.910742	-0.82057	2.759208
935	1	6.276612	2.808425	2.73842	1002	1	8.914298	-1.39655	2.990764
936	5	7.32382	0.568995	3.722702	1003	6	-4.82873	-1.24691	1.770213
937	1	7.886741	1.007264	4.668538	1004	6	-3.79761	-3.28527	2.590249
938	5	7.885817	0.796858	2.047406	1005	1	-2.90638	-3.86019	2.803041
939	1	8.873931	1.402023	1.837134	1006	6	-5.06401	-3.77752	3.047634
940	6	-4.76277	0.161622	1.364061	1007	6	-6.22209	-3.05698	2.640285
941	6	-4.11488	1.927517	-0.18283	1008	1	-7.19896	-3.47614	2.850259
942	1	-3.58313	2.215373	-1.07949	3459	17	-1.09204	0.586091	4.686834
943	6	-4.89899	2.870214	0.506284	3460	6	-1.1606	0.568206	2.874714
944	6	-5.54168	2.453569	1.688043	3461	1	-2.2009	0.396841	2.607179
945	1	-6.11023	3.161963	2.277767	3462	1	-0.85609	1.552512	2.525738
946	6	-6.09658	-1.80845	2.081758	3463	17	-0.46645	-0.68856	0.544407
947	1	-6.97472	-1.21611	1.872232	3464	6	-0.24848	-0.52455	2.350939
948	6	-5.17822	-4.92632	3.934949	3465	1	-0.48752	-1.49537	2.780906
949	6	-3.23499	-6.13101	4.887409	3466	1	0.803055	-0.3003	2.519367

Table S13. Optimized geometry of QM/MM-treated **CB3Ph6** in **DBE@CB3Ph6** at the S_1 ICT state

Center Number	Atomic Number	Coordinates (Angstroms)			Center Number	Atomic Number	Coordinates (Angstroms)		
		x	y	z			x	y	z
3151	6	4.937112	-0.61822	2.016002	3218	1	4.691456	2.092376	5.799873
3152	6	4.558638	-0.7549	0.661434	3219	6	5.17909	3.21245	4.01466
3153	1	4.20527	0.109662	0.111183	3220	6	5.356107	3.084998	2.615921
3154	6	4.602266	-1.9858	0.01339	3221	1	5.618469	3.959412	2.043814
3155	1	4.302315	-2.04322	-1.02558	3222	6	5.229764	1.869487	1.975103
3156	6	5.04606	-3.13649	0.685805	3223	1	5.364006	1.83162	0.903218
3157	6	5.423309	-3.00378	2.031698	3224	6	5.308374	4.512581	4.65573
3158	1	5.813219	-3.85657	2.564634	3225	6	3.447805	5.877938	5.069784
3159	6	5.355627	-1.7857	2.68449	3226	6	2.099639	5.377395	4.749443
3160	1	5.671727	-1.73691	3.716423	3227	6	1.623346	5.326264	3.412191
3161	6	5.189368	-4.47412	0.016843	3228	1	2.20791	5.782504	2.624298
3162	6	3.774987	-5.46105	-0.28616	3229	6	0.477807	4.629889	3.086759
3163	6	2.42453	-4.8813	0.071219	3230	1	0.200183	4.553212	2.04146
3164	6	2.057593	-4.61944	1.401584	3231	6	-0.28567	3.954353	4.081568
3165	1	2.724071	-4.87299	2.215075	3232	6	0.122365	4.125989	5.434778
3166	6	0.849771	-3.9958	1.707171	3233	1	-0.47107	3.701024	6.235396
3167	1	0.638526	-3.76333	2.746271	3234	6	1.261593	4.832173	5.760503
3168	6	-0.05667	-3.61721	0.702206	3235	1	1.553139	4.934143	6.799516
3169	6	0.284033	-3.9454	-0.62258	3236	6	-1.42495	3.122029	3.726399
3170	1	-0.3985	-3.71779	-1.43373	3237	6	-2.10131	3.279623	2.485208
3171	6	1.499369	-4.55388	-0.93324	3238	1	-1.78013	4.042704	1.786757
3172	1	1.726517	-4.76888	-1.97142	3239	6	-3.21494	2.523976	2.171589
3173	6	-1.30082	-2.87253	1.037989	3240	1	-3.72445	2.702044	1.235462
3174	6	-1.96194	-3.06556	2.266214	3241	6	-3.71442	1.551284	3.062073
3175	1	-1.59267	-3.80294	2.971795	3242	6	-3.03163	1.358959	4.279725
3176	6	-3.12067	-2.36282	2.584713	3243	1	-3.38351	0.614212	4.980305
3177	1	-3.6142	-2.56827	3.524833	3244	6	-1.92355	2.121833	4.606716
3178	6	-3.6722	-1.42637	1.694594	3245	1	-1.42831	1.9341	5.552262
3179	6	-3.0161	-1.2279	0.470594	3246	6	-4.99927	0.83566	2.760756
3180	1	-3.41836	-0.52587	-0.24641	3247	5	4.624474	5.958706	3.844371
3181	6	-1.8574	-1.93358	0.150053	3248	1	4.279381	5.818752	2.720335
3182	1	-1.37784	-1.73622	-0.80277	3249	5	4.443689	4.904736	6.118036
3183	6	-4.98484	-0.75053	2.003575	3250	1	3.917931	4.020502	6.709708
3184	5	4.852828	-5.88489	0.983037	3251	5	6.374749	5.665676	4.248428
3185	1	4.49899	-5.73533	2.092748	3252	1	7.149152	5.362245	3.408398
3186	5	4.649115	-4.7089	-1.59527	3253	5	6.268958	4.926842	5.904006
3187	1	4.123907	-3.81938	-2.16218	3254	1	6.968372	4.080255	6.347178
3188	5	6.488382	-5.48216	0.43479	3255	5	3.88796	6.619569	6.45581
3189	1	7.238812	-5.04086	1.229188	3256	1	3.034084	6.801923	7.256846
3190	5	6.377595	-4.76552	-1.18323	3257	5	4.020079	7.400134	4.831843
3191	1	7.051724	-3.85019	-1.49878	3258	1	3.267775	8.199869	4.38343
3192	5	4.045495	-6.37278	-1.70006	3259	5	5.721483	7.30663	4.346936
3193	1	3.112499	-6.55721	-2.39807	3260	1	6.160046	8.124276	3.611476
3194	5	4.17417	-7.11971	-0.09253	3261	5	5.513472	6.131644	6.947549
3195	1	3.323312	-7.82101	0.333755	3262	1	5.804071	6.126987	8.093374
3196	5	5.895483	-7.15599	0.357076	3263	5	6.686024	6.658209	5.708131
3197	1	6.320096	-7.98816	1.082266	3264	1	7.787163	7.018549	5.968655
3198	5	5.685975	-5.981	-2.26368	3265	5	5.281556	7.663914	6.054699
3199	1	5.988079	-6.00385	-3.40448	3266	1	5.409043	8.73049	6.552996
3200	5	6.834737	-6.47307	-0.99758	3267	5	-5.43237	-0.56434	3.668819
3201	1	7.9364	-6.82953	-1.25019	3268	1	-4.69374	-0.95835	4.497131
3202	5	5.400637	-7.46626	-1.32631	3269	5	-6.35512	1.72221	2.216362
3203	1	5.47475	-8.5373	-1.81516	3270	1	-6.216	2.891523	2.113185
3204	5	-5.46087	0.651636	1.105483	3271	5	-6.33911	0.958548	3.825036
3205	1	-4.73948	1.06132	0.269346	3272	1	-6.17962	1.601671	4.805386
3206	5	-6.3235	-1.64579	2.570977	3273	5	-7.19669	-0.59193	3.708449
3207	1	-6.17255	-2.81341	2.671659	3274	1	-7.76079	-1.04691	4.645798
3208	5	-6.34525	-0.88209	0.964838	3275	5	-7.77689	0.830929	2.786717
3209	1	-6.20092	-1.51919	-0.02096	3276	1	-8.77208	1.410476	3.049563
3210	5	-7.22689	0.655006	1.094271	3603	6	1.33577	0.538408	3.179147
3211	1	-7.81038	1.100423	0.164334	3604	1	2.322256	0.994298	3.159342
3212	5	-7.76932	-0.76901	2.028138	3605	1	0.57108	1.27294	3.413684
3213	1	-8.7633	-1.35766	1.790397	3606	35	1.367113	-0.72157	4.699572
3214	6	4.967915	0.683655	2.694909	3607	6	1.019056	-0.23874	1.930803
3215	6	4.788343	0.804552	4.09354	3608	1	1.769754	-0.99199	1.704703
3216	1	4.547555	-0.07424	4.67969	3609	1	0.025111	-0.67669	1.954738
3217	6	4.866624	2.032102	4.732731	3610	35	1.010372	0.987336	0.38198

Table S14. Optimized geometry of QM/MM-treated **CB3Ph6** in **DBE@CB3Ph6** at the S_1 dark state

Center Number	Atomic Number	Coordinates (Angstroms)			Center Number	Atomic Number	Coordinates (Angstroms)		
		x	y	z			x	y	z
3151	6	4.762705	-0.19475	1.364895	3218	1	7.189525	3.428406	2.898254
3152	6	4.036811	-0.62057	0.234556	3219	6	5.052512	3.728438	3.078703
3153	1	3.42668	0.086704	-0.3164	3220	6	3.790477	3.241554	2.605298
3154	6	4.145198	-1.93014	-0.2253	3221	1	2.898355	3.818521	2.808492
3155	1	3.637499	-2.20271	-1.14019	3222	6	3.683086	2.033233	1.952804
3156	6	4.908233	-2.88596	0.468677	3223	1	2.717368	1.702944	1.590683
3157	6	5.526283	-2.49195	1.67041	3224	6	5.160863	4.863652	3.982654
3158	1	6.078906	-3.21263	2.260572	3225	6	3.223483	6.073475	4.938144
3159	6	5.483374	-1.16935	2.091129	3226	6	1.881006	5.559285	4.667131
3160	1	6.004074	-0.88443	2.999325	3227	6	1.323002	5.553193	3.371238
3161	6	5.114489	-4.29019	-0.05405	3228	1	1.816078	6.09118	2.573414
3162	6	3.74065	-5.34587	-0.22147	3229	6	0.210487	4.780885	3.065606
3163	6	2.37108	-4.81202	0.125016	3230	1	-0.12836	4.767158	2.035441
3164	6	1.961425	-4.63618	1.456412	3231	6	-0.43331	3.997023	4.042839
3165	1	2.607044	-4.92888	2.273937	3232	6	0.039483	4.118579	5.364667
3166	6	0.737409	-4.04637	1.761021	3233	1	-0.47266	3.611823	6.174276
3167	1	0.495587	-3.88454	2.80657	3234	6	1.166791	4.865612	5.670444
3168	6	-0.14606	-3.62183	0.752816	3235	1	1.523525	4.894687	6.694195
3169	6	0.228868	-3.89203	-0.57617	3236	6	-1.57892	3.123236	3.702158
3170	1	-0.43829	-3.64039	-1.39221	3237	6	-2.26183	3.267625	2.480513
3171	6	1.460415	-4.46611	-0.88561	3238	1	-1.96449	4.03669	1.778347
3172	1	1.710835	-4.63868	-1.92666	3239	6	-3.36175	2.484386	2.16455
3173	6	-1.39738	-2.8861	1.085497	3240	1	-3.86533	2.646137	1.222324
3174	6	-2.04198	-3.05428	2.325981	3241	6	-3.84491	1.518877	3.058213
3175	1	-1.66064	-3.76974	3.047683	3242	6	-3.16882	1.357588	4.27584
3176	6	-3.2058	-2.35724	2.637454	3243	1	-3.52329	0.635515	4.999599
3177	1	-3.68497	-2.53828	3.589074	3244	6	-2.05675	2.135248	4.585891
3178	6	-3.7765	-1.44948	1.731484	3245	1	-1.57152	1.974113	5.542521
3179	6	-3.13222	-1.26945	0.499532	3246	6	-5.12633	0.79636	2.764601
3180	1	-3.5469	-0.58677	-0.22939	3247	5	4.37274	6.323049	3.653637
3181	6	-1.97	-1.97063	0.184356	3248	1	3.96691	6.444482	2.54675
3182	1	-1.49878	-1.78066	-0.7738	3249	5	4.375992	4.842475	5.490454
3183	6	-5.09793	-0.78526	2.032897	3250	1	3.905604	3.80775	5.831563
3184	5	4.871439	-5.59649	1.05683	3251	5	6.273122	6.056644	3.832792
3185	1	4.542503	-5.31376	2.147494	3252	1	6.963449	6.024091	2.876816
3186	5	4.550327	-4.70539	-1.62669	3253	5	6.268862	4.944056	5.212554
3187	1	3.994237	-3.89145	-2.27097	3254	1	6.975862	4.005744	5.370982
3188	5	6.479339	-5.20817	0.417072	3255	5	3.866044	6.419882	6.376264
3189	1	7.258364	-4.68651	1.134452	3256	1	3.142564	6.440202	7.316985
3190	5	6.28822	-4.6578	-1.2566	3257	5	3.895095	7.551049	4.958317
3191	1	6.923274	-3.76191	-1.68736	3258	1	3.199139	8.474962	4.715145
3192	5	4.004531	-6.38695	-1.54487	3259	5	5.562745	7.571065	4.359531
3193	1	3.051211	-6.66093	-2.18086	3260	1	5.93739	8.545716	3.808417
3194	5	4.202602	-6.95757	0.128152	3261	5	5.525581	5.791439	6.567663
3195	1	3.378343	-7.63548	0.634559	3262	1	5.853478	5.470941	7.65599
3196	5	5.934773	-6.89734	0.526671	3263	5	6.634656	6.653723	5.460232
3197	1	6.407776	-7.63387	1.32122	3264	1	7.727417	7.002381	5.76648
3198	5	5.61219	-6.00058	-2.19361	3265	5	5.245291	7.51319	6.1236
3199	1	5.884183	-6.11869	-3.33587	3266	1	5.419804	8.425365	6.861297
3200	5	6.810692	-6.32473	-0.92122	3267	5	-5.552	-0.59154	3.691539
3201	1	7.917828	-6.66123	-1.17534	3268	1	-4.81284	-0.96891	4.527013
3202	5	5.403954	-7.39692	-1.10386	3269	5	-6.48779	1.662338	2.20177
3203	1	5.490041	-8.51273	-1.48691	3270	1	-6.36066	2.830718	2.078813
3204	5	-5.58387	0.587236	1.108543	3271	5	-6.47176	0.92423	3.81908
3205	1	-4.86473	0.990105	0.267521	3272	1	-6.32386	1.585528	4.788737
3206	5	-6.42536	-1.69561	2.603558	3273	5	-7.31269	-0.63464	3.723637
3207	1	-6.2609	-2.86083	2.715523	3274	1	-7.87383	-1.08487	4.664898
3208	5	-6.45202	-0.95744	0.988698	3275	5	-7.90253	0.766374	2.778151
3209	1	-6.29708	-1.6114	0.014897	3276	1	-8.90604	1.337962	3.023087
3210	5	-7.34588	0.572544	1.092583	3603	6	0.779051	0.356944	3.421209
3211	1	-7.92718	0.999351	0.152729	3604	1	1.268857	1.326295	3.459237
3212	5	-7.87568	-0.84209	2.045852	3605	1	-0.26216	0.454773	3.715582
3213	1	-8.86445	-1.44194	1.823932	3606	35	1.674312	-0.73484	4.800204
3214	6	4.82856	1.208247	1.786411	3607	6	0.945729	-0.35505	2.105607
3215	6	6.093909	1.765963	2.108955	3608	1	1.981947	-0.60268	1.895904
3216	1	6.972981	1.174474	1.901013	3609	1	0.326108	-1.24309	2.0411
3217	6	6.214572	3.010921	2.676339	3610	35	0.366347	0.800211	0.60664

Calculated Electronic Transitions

Table S15. Electronic transitions for the optimized structure of **CB3Ph6** at the S_0 state

Excited State	Spin Multiplicity	Energy / eV	Wavelength / nm	*f*	Composition	Coefficient
1	Singlet-A	4.0865	303.4	0.0001		
					HOMO-2 -> LUMO+2	0.1302
					HOMO-1 -> LUMO+1	-0.48582
					HOMO -> LUMO	0.49023
2	Singlet-A	4.2754	289.99	0.3521		
					HOMO-1 -> LUMO	-0.45729
					HOMO -> LUMO+1	0.51431
3	Singlet-A	4.2756	289.98	0.3653		
					HOMO-2 -> LUMO	0.10805
					HOMO-1 -> LUMO+1	0.48801
					HOMO -> LUMO	0.4814
4	Singlet-A	4.2831	289.47	0.0015		
					HOMO-1 -> LUMO	0.52234
					HOMO -> LUMO+1	0.46767
5	Singlet-A	4.3193	287.05	0.44		
					HOMO-2 -> LUMO	0.6828
					HOMO -> LUMO+2	-0.1219
6	Singlet-A	4.3199	287.01	0.4499		
					HOMO-2 -> LUMO+1	0.68489
					HOMO-1 -> LUMO+2	0.12199

Table S16. Electronic transitions for the optimized structure of **CB3Ph6** at the S_1 ICT state

Excited State	Spin Multiplicity	Energy / eV	Wavelength / nm	*f*	Composition	Coefficient
1	Singlet-A	2.5778	480.97	0.3588		
					HOMO -> LUMO	0.70032

Table S17. Electronic transitions for the optimized structure of **CB3Ph6** at the S_1 dark state

Excited State	Spin Multiplicity	Energy / eV	Wavelength / nm	*f*	Composition	Coefficient
1	Singlet-A	1.6844	736.06	0.0027		
					HOMO-5 -> LUMO	-0.12026
					HOMO -> LUMO	-0.69403

Table S18. Electronic transitions for the optimized structure of QM/MM-treated **CB3Ph6** in **CB3Ph6**α at the S_1 ICT state

Excited State	Spin Multiplicity	Energy / eV	Wavelength / nm	*f*	Composition	Coefficient
1	Singlet-A	2.5825	480.1	0.298		
					HOMO -> LUMO	-0.70066

Table S19. Electronic transitions for the optimized structure of QM/MM-treated **CB3Ph6** in **CB3Ph6**α at the S_1 dark state

Excited State	Spin Multiplicity	Energy / eV	Wavelength / nm	*f*	Composition	Coefficient
1	Singlet-A	1.8748	661.33	0.001		
					HOMO-5 -> LUMO	0.1009
					HOMO -> LUMO	-0.69402

Table S20. Electronic transitions for the optimized structure of QM/MM-treated **CB3Ph6** in **DCE@CB3Ph6** at the S_1 ICT state

Excited State	Spin Multiplicity	Energy / eV	Wavelength / nm	*f*	Composition	Coefficient
1	Singlet-A	2.6027	476.37	0.3101		
					HOMO -> LUMO	0.69946

Table S21. Electronic transitions for the optimized structure of QM/MM-treated **CB3Ph6** in **DCE@CB3Ph6** at the S_1 dark state

Excited State	Spin Multiplicity	Energy / eV	Wavelength / nm	*f*	Composition	Coefficient
1	Singlet-A	1.8147	683.24	0.0016		
					HOMO-5 -> LUMO	-0.11021
					HOMO -> LUMO	0.69369

Table S22. Electronic transitions for the optimized structure of QM/MM-treated **CB3Ph6** in **DBE@CB3Ph6** at the S_1 ICT state

Excited State	Spin Multiplicity	Energy / eV	Wavelength / nm	*f*	Composition	Coefficient
1	Singlet-A	2.6148	474.17	0.2915		
					HOMO -> LUMO	-0.70007

Table S23. Electronic transitions for the optimized structure of QM/MM-treated **CB3Ph6** in **DBE@CB3Ph6** at the S_1 dark state

Excited State	Spin Multiplicity	Energy / eV	Wavelength / nm	*f*	Composition	Coefficient
1	Singlet-A	1.8172	682.27	0.0018		
					HOMO -> LUMO	0.69357

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