Electronic Supplementary Information

Heavy-Atom-Free Amorphous Materials with Facile Preparation and Efficient Room-Temperature Phosphorescence Emission

Changxing Zhao, Yanhuan Jin, Jie Wang, Xiaoming Cao, Xiang Ma* and He Tian
Key Laboratory for Advanced Materials and Feringa Nobel Prize Scientist Joint Research Center, Institute of Fine Chemicals, School of Chemistry and Molecular Engineering, East China University of Science & Technology, 130 Meilong Road, Shanghai, 200237, China. E-mail: maxiang@ecust.edu.cn.

Materials, general procedures and synthesis.

Materials. Mono[6-O-(4-methyl-phenylsulfonyl)]-β-cyclodextrin (6-OTs-β-CD) was synthesized according to literature procedure.[1] β-cyclodextrin, methyl 4-hydroxybenzoate, 4-hydroxybenzaldehyde, 4-hydroxyacetophenone and tert-butyl-4-hydroxybenzoate were purchased from J&K chemical Ltd. SiliaSphere C18 was purchased from Beijing Greenherbs science and technology development Ltd. All other reagents were commercially available and used as supplied without further purification. Solvents were purified according to standard laboratory methods. The molecular structures were confirmed using ^{1}H NMR, ^{13}C NMR and high-resolution ESI mass spectroscopy or MALDI-TOF mass spectroscopy.

General. ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker AV-400 spectrometer. The UV-Vis absorption spectra were obtained on a Varian Cary 100 spectrometer (1 cm quartz cell was used). RTP spectra and lifetime were recorded on a Varian Cary Eclipse spectrophotometer. Phosphorescence mode: Excitation slit = 10 nm; Emission slit = 10 nm; Delay time = 0.1 ms; Gate time = 2.0 ms. Quantum yields were determined with a spectrometer C11347-11 (Hamamatsu, Japan), Powder X-ray diffraction (XRD) was performed on a D/max2550V. The calculations were performed with the Gaussian 09 software package. The restricted and unrestricted (TD)B3LYP functional and the 6-311+G(d) basis set was used for both DFT and TDDFT calculations[2-4]. The lowest excitation states were included in the TDDFT calculations.

Synthesis

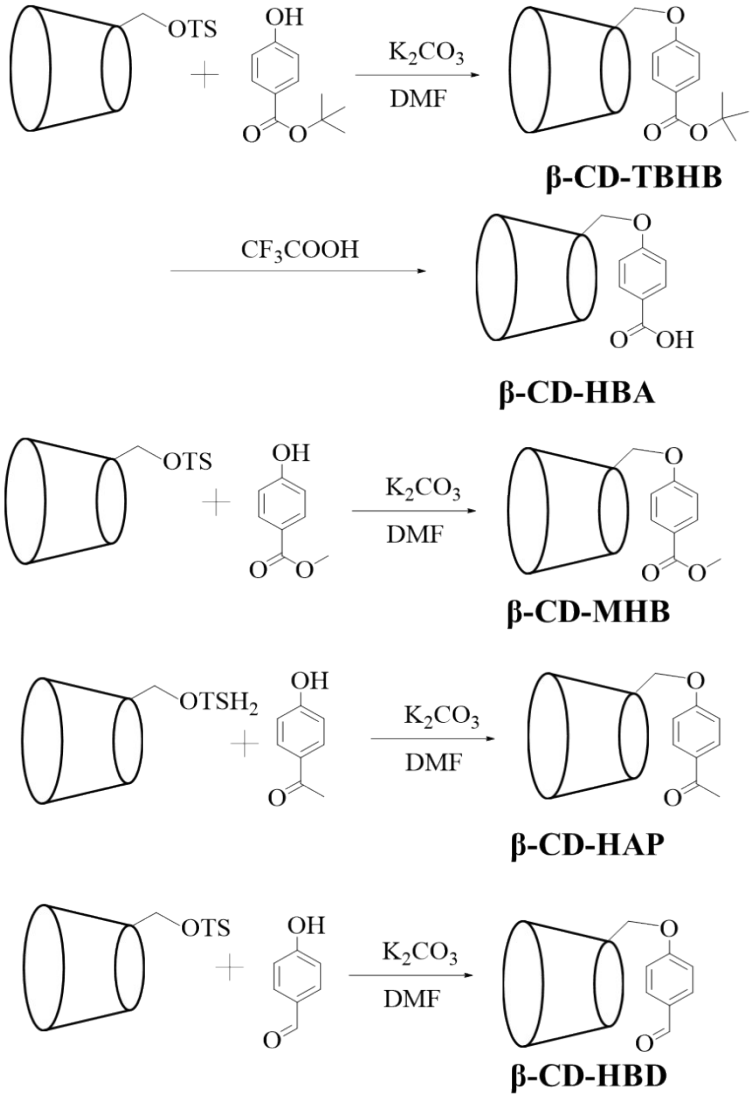

Figure S1. Synthesis of β-CD-HBA, β-CD-MHB, β-CD-HAP, β-CD-HBD.

Synthesis of tert-butyl 4-hydroxybenzoate modified β-cyclodextrin (β-CD-TBHB) To a stirred solution of 6-OTs-β-CD (0.5 g, 0.39 mmol, 1.0 eq) and K_2CO_3 (0.27g, 1.95 mmol, 5.0 eq) in 20 mL dry DMF was added tert-butyl 4-hydroxybenzoate (0.379 g, 1.95 mmol, 5.0 eq). The mixture was stirred at 80 °C under argon for 3 days and filtered after cooled to room temperature. The solution was concentrated into 3 mL and added dropwise to 200 mL ethyl acetate to afford the crude product, then purified with SiliaSphere C18 reversed-phase column chromatography to obtain β-CD-TBHB (0.3 g, 59%). ^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.86 – 7.78 (m, 2H), 7.05 – 6.96 (d, *J*=8.7, 2H), 5.85 – 5.64 (m, 14H), 4.95 – 4.75 (m, 7H), 4.54 – 4.40 (ddt, *J*=17.1, 10.5, 5.3, 6H), 3.80 – 3.44 (m, overlaps with HOD), 1.56 – 1.50 (s, 9H). ^{13}C NMR (101 MHz, DMSO-d_6) δ = 164.74 – 164.58, 162.07 – 161.87, 131.12 – 130.65 , 123.60 – 123.27, 114.44 – 113.93, 103.38 – 100.83, 81.63 – 81.28, 80.21 – 79.91, 73.14 – 72.81, 72.48

– 72.28, 72.28 – 72.19, 72.09 – 71.85, 60.88 – 58.96, 30.30 – 26.06. HRMS (MALDI-TOF-MS) m/z: $[M + Na]^+$ calcd for $[C_{50}H_{76}NaO_{37}]^+$, 1333.4427; found, 1333.4380.

Synthesis of 4-hydroxybenzoic acid modified β-cyclodextrin (β-CD-HBA) β-CD-TBHB (0.2 g, 0.15 mmol) and trifluoroacetic acid (2 ml) were added into a flask containing 15ml DMF. The mixture was stirred at room temperature for 20 hours. The solution was concentrated into 3 mL and added dropwise to 200 mL ethyl acetate to afford the crude product, then purified with SiliaSphere C18 reversed-phase column chromatography to obtain β-CD-HBA (0.1 g, 52%). ^{1}H NMR (400 MHz, DMSO-d_6) δ = 9.88 – 9.85 (s, 1H), 7.88 – 7.82 (m, 2H), 7.16 – 7.11 (d, *J*=8.9, 2H), 5.81 – 5.68 (m, 15H), 4.92 – 4.79 (m, 7H), 4.52 – 4.41 (m, 6H), 3.76 – 3.45 (m, overlaps with HOD). ^{13}C NMR (101 MHz, DMSO-d_6) δ = 167.11 – 166.85, 162.45 – 162.15, 131.78 – 130.76, 123.63 – 121.98, 115.12 – 113.47, 102.55 – 101.39, 81.69 – 81.20, 73.09 – 72.79, 72.52 – 72.28, 72.28 – 72.15, 72.09 – 71.88, 60.04 – 59.58. HRMS (MALDI-TOF-MS) m/z: $[M - H]^-$ calcd for $[C_{50}H_{75}NaO_{37}]^-$, 1253.3836; found, 1253.3838.

Synthesis of Methyl 4-hydroxybenzoate modified β-cyclodextrin (β-CD-MHB) To a stirred solution of 6-OTs-β-CD (0.5 g, 0.39 mmol, 1.0 eq) and K_2CO_3 (0.27g, 1.95 mmol, 5.0 eq) in 20 mL dry DMF was added Methyl 4-hydroxybenzoate (0.297 g, 1.95 mmol, 5.0 eq). The mixture was stirred at 80 ℃ under argon for 3 days and filtered after cooled to room temperature. The solution was concentrated into 3 mL and added dropwise to 200 mL ethyl acetate to afford the crude product, then purified with SiliaSphere C18 reversed-phase column chromatography to obtain β-CD-MHB (0.28 g, 56.8%). ^{1}H NMR (400 MHz, DMSO-d_6) δ= 7.92 – 7.86 (d, *J*=8.4, 2H), 7.08 – 7.02 (d, *J*=8.4, 2H), 5.81 – 5.67 (m, 14H), 4.91 – 4.77 (m, 7H), 4.52 – 4.38 (m, 6H), 3.81 (s, 3H), 3.77 – 3.36 (m, overlaps with HOD). ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.92 , 162.36 , 131.11 , 121.78 , 114.46 , 101.91, 82.10,81.78 , 81.50 , 73.00 , 72.36 , 72.22, 71.99, 67.21 , 59.87, 51.77. HRMS (MALDI-TOF-MS) m/z: $[M + Na]^+$ calcd for $[C_{50}H_{76}NaO_{37}]^+$, 1291.3958; found, 1291.3953.

Synthesis of 4-hydroxyacetophenone modified β-cyclodextrin (β-CD-HAP) To a stirred solution of 6-OTs-β-CD (0.5 g, 0.39 mmol, 1.0 eq) and K_2CO_3 (0.27g, 1.95 mmol, 5.0 eq) in 20 mL dry DMF was added 4-Hydroxyacetophenone (0.266 g, 1.95 mmol, 5.0 eq). The mixture was stirred at 80 ℃ under argon for 3 days and filtered after cooled to room temperature. The solution was concentrated into 3 mL and added dropwise to 200 mL ethyl acetate to afford the crude product, then purified with SiliaSphere C18 reversed-phase column chromatography to obtain β-CD-PHAP (0.28 g, 56.8%). ^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.94 – 7.88 (d, *J*=8.4, 2H), 7.08 – 7.01 (d, *J*=8.8, 2H), 5.83 – 5.68 (m, 14H), 4.92 – 4.78 (m, 7H), 4.55 – 4.39 (m, 6H), 3.76 – 3.36 (m, overlaps with HOD), 2.54-2.43 (s, overlaps with DMSO-d_6).^{13}C NMR (100 MHz, DMSO-d_6) δ 196.35, 162.26, 130.37, 129.83, 114.29, 102.34, 101.92, 101.74, 82.06,

81.78, 81.50, 73.01, 72.36, 72.22, 71.99, 69.42, 67.16, 59.88, 26.35. HRMS (MALDI-TOF-MS) m/z: $[M + Na]^+$ calcd for $[C_{50}H_{76}NaO_{36}]^+$, 1275.4008; found, 1275.4010.

Synthesis of 4-hydroxybenzaldehyde modified β-cyclodextrin (β-CD-HBD) To a stirred solution of 6-OTs-β-CD (0.5 g, 0.39 mmol, 1.0 eq) and K_2CO_3 (0.27 g, 1.95 mmol, 5.0 eq) in 20 mL dry DMF was added 4-hydroxy benzaldehyde (0.238 g, 1.95 mmol, 5.0 eq). The mixture was stirred at 80 ℃ under argon for 3 days and filtered after cooled to room temperature. The solution was concentrated into 3 mL and added dropwise to 200 mL ethyl acetate to afford the crude product, then purified with SiliaSphere C18 reversed-phase column chromatography to obtain β-CD-PHAP (0.25 g, 52%).^{1}H NMR (400 MHz, DMSO-d_6) δ = 9.88 – 9.85 (s, 1H), 7.88 – 7.82 (d, J=8.4, 2H), 7.16 – 7.11 (d, J=8.9, 2H), 5.81 – 5.68 (m, 14H), 4.92 – 4.79 (m, 7H), 4.52 – 4.41 (m, 6H), 3.76 – 3.45 (m, overlaps with HOD). ^{13}C NMR (100 MHz, DMSO-d_6) δ 191.33, 163.39, 162.35, 131.70, 129.59, 114.97, 102.34, 101.91, 82.09, 81.78, 81.52, 73.01, 72.36, 72.20, 71.99, 69.37, 67.36, 59.88. HRMS (MALDI-TOF-MS) m/z: $[M + Na]^+$ calcd for $[C_{49}H_{74}NaO_{36}]^+$, 1261.3852; found, 1261.3845.

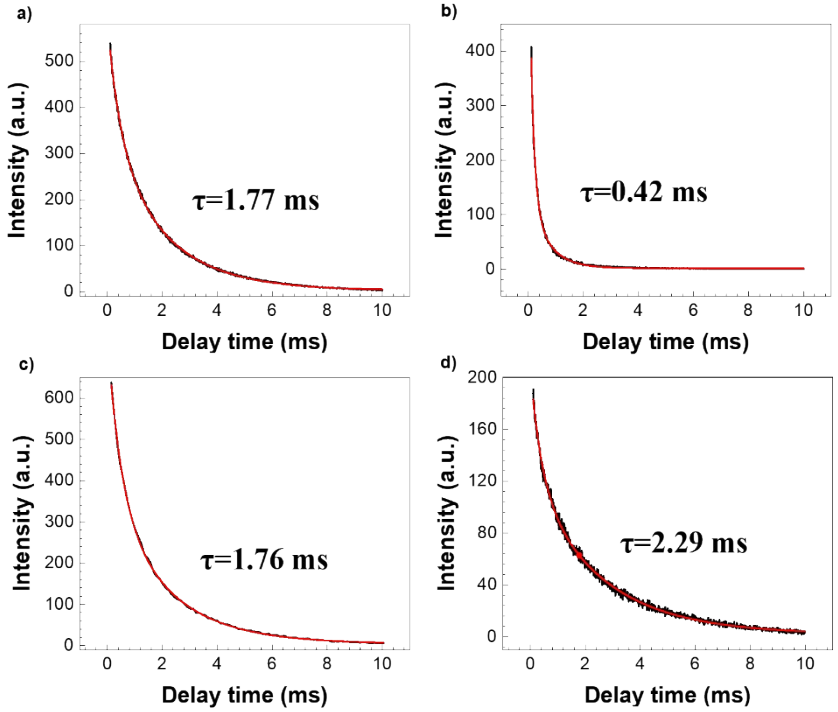

Figure S2. RTP lifetime spectra of a) β-CD-HAP, b) β-CD-HBD, c) β-CD-MHB and d) β-CD-HBA in solid state at room temperature, registered in gate mode. a) λ_{em} = 437 nm, b) λ_{em} = 447 nm, c) λ_{em} = 424 nm and d) λ_{em} = 419 nm, excitation voltage = 800 V, excitation slim =20 nm, emission slim = 20 nm.

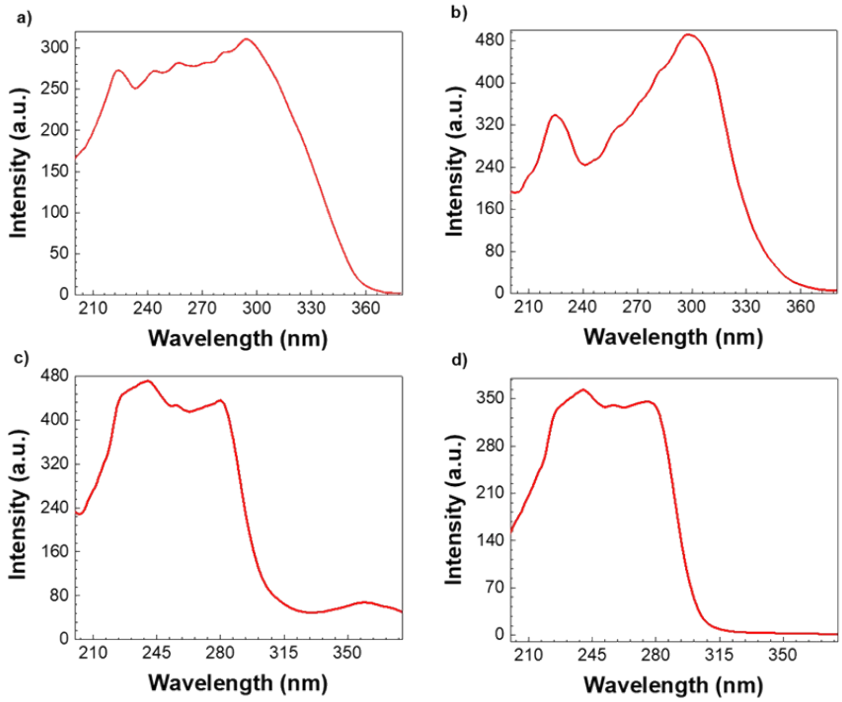

Figure S3. RTP excitation spectra of a) β-CD-HAP, b) β-CD-HBD, c) β-CD-MHB and d) β-CD-HBA in solid state at room temperature, registered in gate mode. a) λ_{em} = 437 nm, b) λ_{em} = 447 nm, c) λ_{em} = 424 nm and d) λ_{em} = 419 nm, excitation voltage = 600 V (β-CD-HAP),700 V (β-CD-HBD) 750 V (β-CD-MHB) or 800 V (β-CD-HBA), excitation slim =10 nm, emission slim = 10 nm.

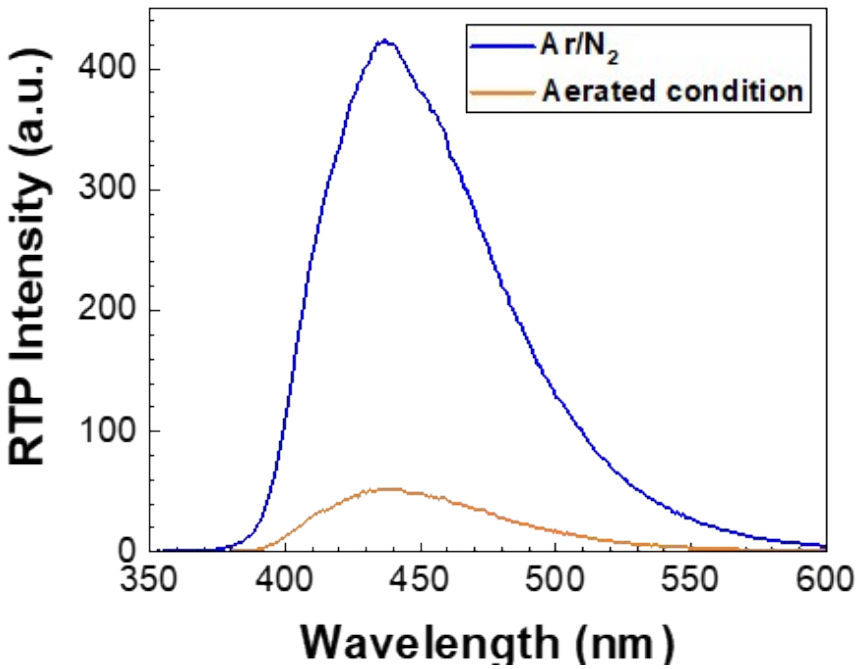

Figure S4. RTP emission spectra of β-CD-HAP in oxygen-free and aerated condition. phosphorescence mode; excitation slim = 10 nm; emission slim = 10 nm; λex = 295 nm, excitation voltage = 600 V.

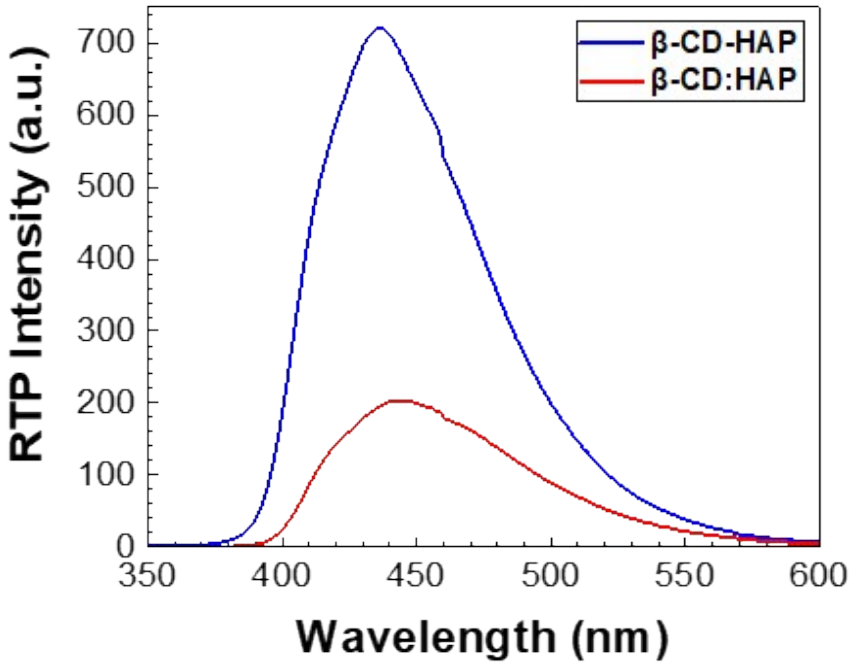

Figure S5. RTP emission spectra of β-CD-HAP and mixtures 4-hydroxyacetophenone : β-CD (molar ratio 1:1) powder prepared from DMF solution. Excitation voltage = 700 V, excitation slim = 10 nm; emission slim = 10 nm; excited at 295 nm.

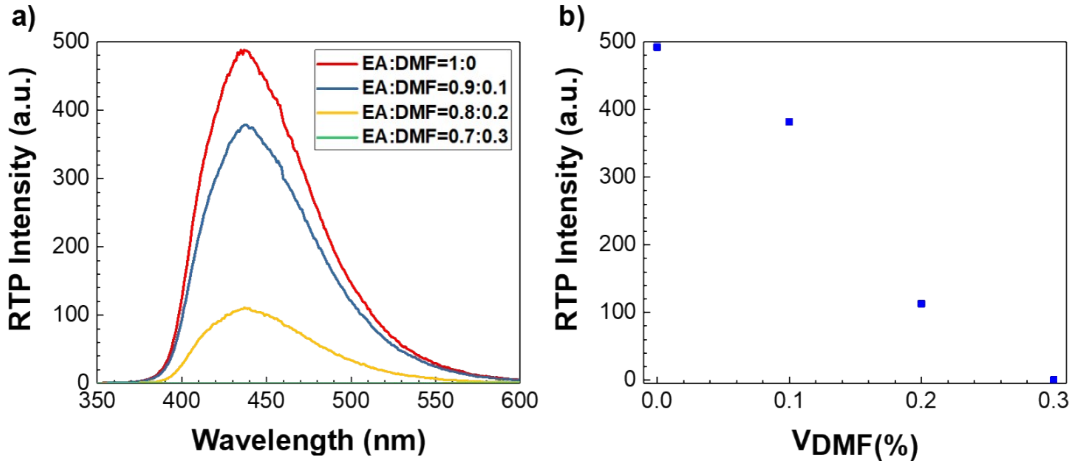

Figure S6. At different volume mixing ratios of DMF/EA, a) RTP emission spectra of β-CD-HAP b) Normalized RTP intensities of β-CD-HAP at 437nm. phosphorescence mode; excitation slim = 10 nm; emission slim = 10 nm; λ_{ex} = 295 nm, excitation voltage = 700 V.

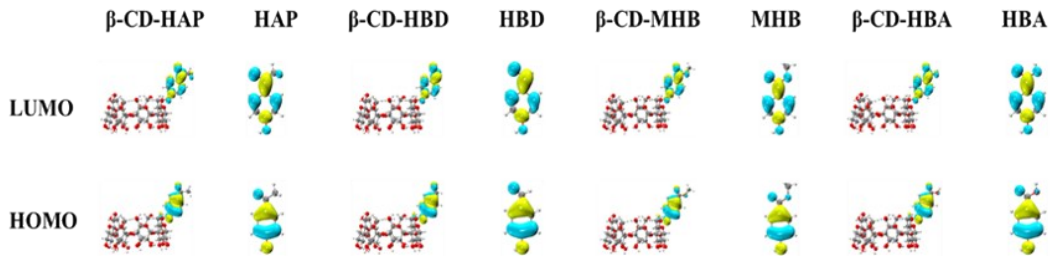

Figure S7. The comparison diagram of calculated HOMO and LUMO for ground states for CD derivatives and their corresponding phosphors.

The shape of frontier molecular orbital for CD derivative kept pace with its corresponding phorsphors, verifying that the electrons of CD was not involved in the efficient spin-orbital coupling.

References

S1. Tian Lu, Feiwu Chen, *J. Comput. Chem.*, 2012, **33**, 580-592.

S2. Humphrey, W., Dalke, A. and Schulten, K., "VMD - Visual Molecular Dynamics", *J. Molec. Graphics,* 1996, **14**, 33-38.

S3. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, Wallingford, CT, 2009.

S4. Becke, A. D.; *J. Chem. Phys.* 1993, **98**, 5648-5652.