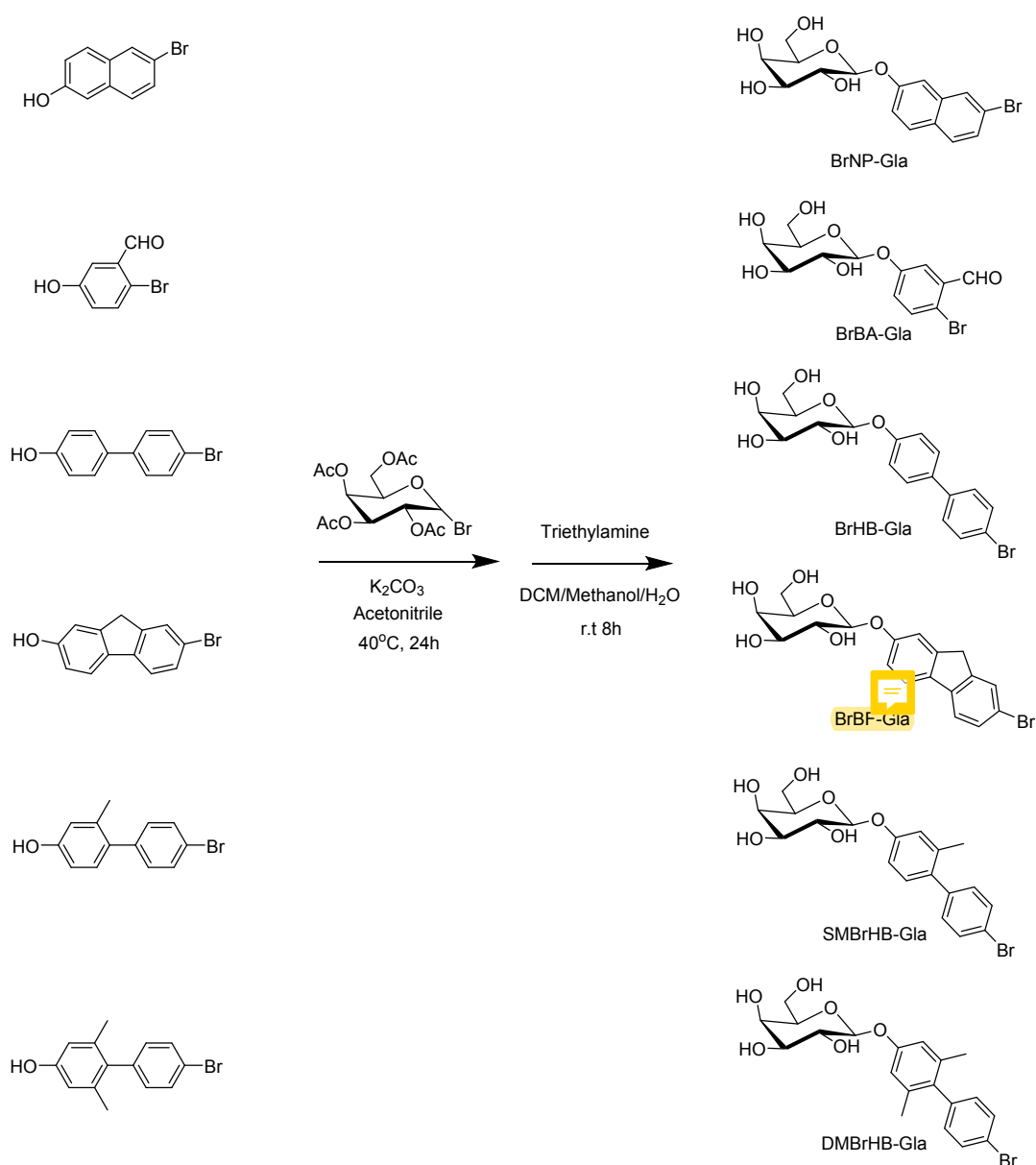


# Conformation-dependent phosphorescence of galactose decorated phosphors and assembling-induced phosphorescence enhancement

*Zhiyi Yuan, Lei Zou, Dongdong Chang and Xiang Ma\**

Key Laboratory for Advanced Materials and Feringa Nobel Prize Scientist Joint Research Center, Frontiers Science Center for Materiobiology and Dynamic Chemistry, School of Chemistry and Molecular Engineering, East China University of Science and Technology, Shanghai 200237, China. E-mail: [maxiang@ecust.edu.cn](mailto:maxiang@ecust.edu.cn).

## Experiment Section



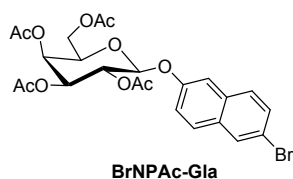
**Scheme S1** General synthesis of BrNP-Gla, BrBA-Gla, BrHB-Gla, BrHF-Gla, SMBrHB-Gla, DMBrHB-Gla.

**Synthesis of BrNP-Gla** 6-bromonaphthalen-2-ol, 2,3,4,6-tetra-O-acetyl- $\alpha$ -D-galactopyranosyl bromide and anhydrous potassium carbonate were dissolved in dry acetonitrile, under the protection of  $N_2$ , the reaction was stirred at  $50^\circ C$  for 24h. The reaction mixture was filtered and washed with DCM. Collect the

filtrate and evaporate the solvent to obtain a crude product of the intermediate product. The crude product was further purified by column chromatography (PE: EA= 3:1) to obtain the intermediate product. Since the difference of polarity between the intermediate product and 2,3,4,6-tetra-O-acetyl- $\alpha$ -D-galactopyranosyl bromide was very little, the intermediate product was not easy to be separate thoroughly, the rude intermediate product was used directly in the next reaction.

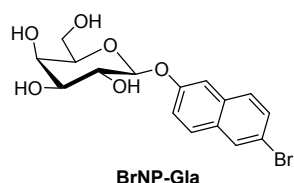
The intermediate product was dissolved in a mixture of dichloromethane/methanol/water (DCM: MeOH: H<sub>2</sub>O=5:4:1), the water should be excess for the reaction. Excess triethylamine was added and the reaction was stirred at room temperature for 12 hours. The mixture was then evaporated to dryness, and the residue was washed by stirred in water and dichloromethane to obtain a pure white solid. The product may further be purified by C18 column chromatography (H<sub>2</sub>O: Metanol= 8: 2).

The synthesis of BrBA-Gla. BrHB-Gla, BrHF-Gla, SBrHB-Gla, DMBrHB-Gla were the same as the synthesis of BrNP-Gla. For SBrHB-Gla and DMBrHB-Gla, which were soluble in dichloromethane, anhydrous ether was used instead of dichloromethane. The characterization of these compounds was as follows:



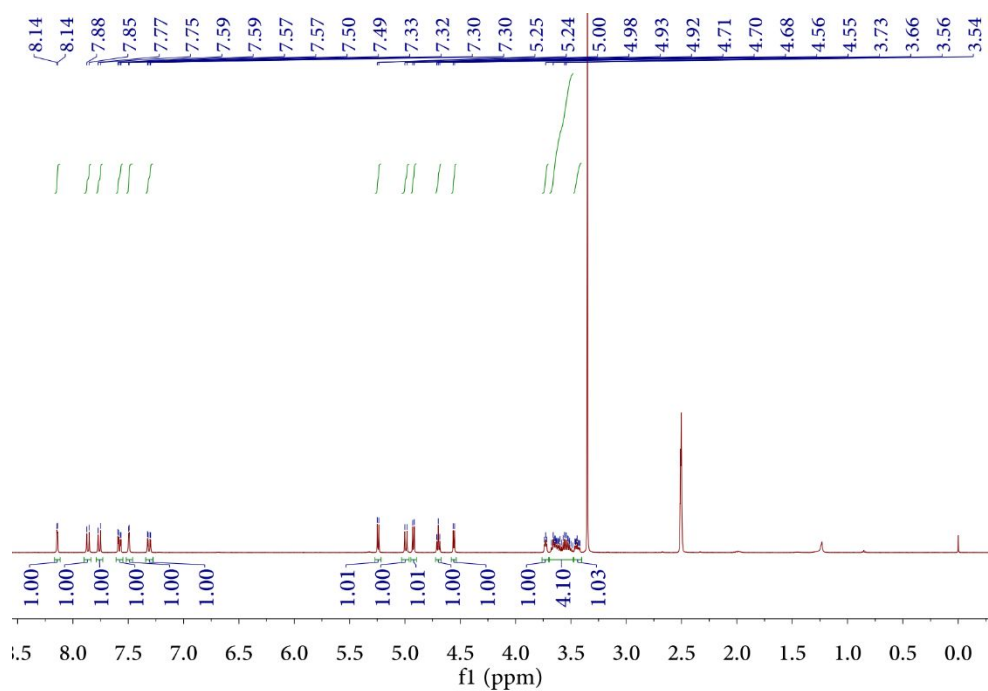
**Scheme S2.** Chemical structure of BrNPAc-Gla

**BrNPAc-Gla**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.96 (d,  $J$  = 1.6 Hz, 1H), 7.69 (d,  $J$  = 9.0 Hz, 1H), 7.61 (d,  $J$  = 8.8 Hz, 1H), 7.54 (dd,  $J$  = 8.7, 1.9 Hz, 1H), 7.32 (d,  $J$  = 2.3 Hz, 1H), 7.22 (dd,  $J$  = 8.9, 2.4 Hz, 1H), 5.53 (ddd,  $J$  = 15.0, 8.3, 5.1 Hz, 2H), 5.22 – 5.12 (m, 2H), 4.22 – 4.06 (m, 3H), 2.20 (s, 3H), 2.09 (s, 3H), 2.07 (s, 3H), 2.03 (s, 3H).

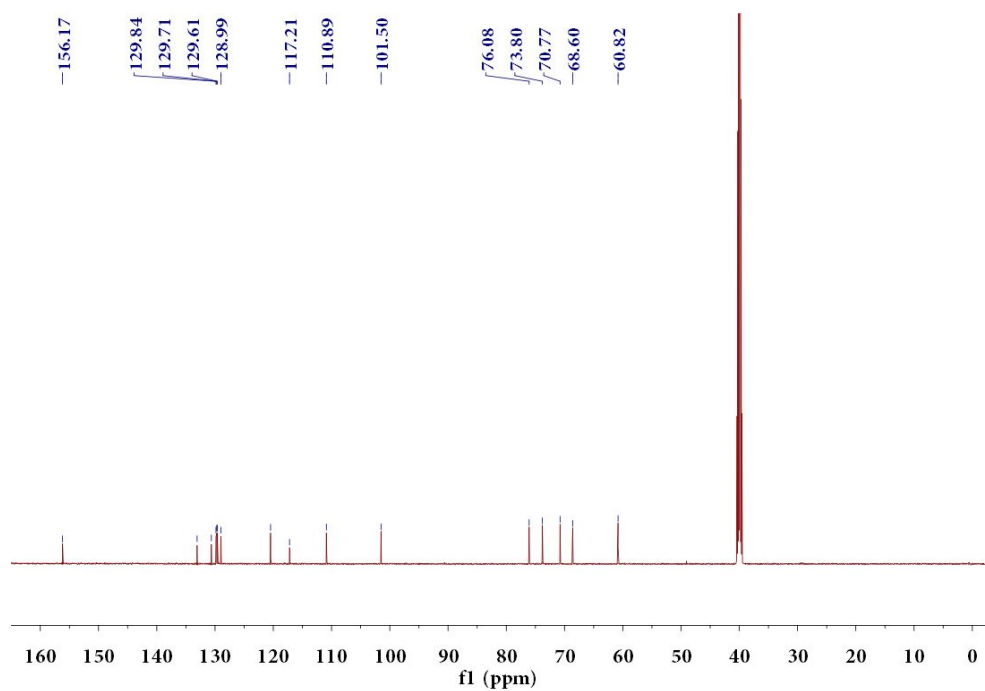


**Scheme S3.** Chemical structure of BrNP-Gla

**BrNP-Gla**  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  8.14 (d,  $J$  = 2.2 Hz, 1H), 7.86 (d,  $J$  = 9.0 Hz, 1H), 7.76 (d,  $J$  = 8.9 Hz, 1H), 7.58 (dd,  $J$  = 8.7, 2.1 Hz, 1H), 7.49 (d,  $J$  = 2.5 Hz, 1H), 7.31 (dd,  $J$  = 8.9, 2.4 Hz, 1H), 5.24 (d,  $J$  = 5.2 Hz, 1H), 4.99 (d,  $J$  = 7.7 Hz, 1H), 4.92 (d,  $J$  = 5.6 Hz, 1H), 4.70 (t,  $J$  = 5.5 Hz, 1H), 4.56 (d,  $J$  = 4.7 Hz, 1H), 3.76 – 3.70 (m, 1H), 3.69 – 3.48 (m, 4H), 3.44 (ddd,  $J$  = 9.3, 5.7, 3.3 Hz, 1H).  $^{13}\text{C}$  NMR (151 MHz, **DMSO**)  $\delta$  156.17, 133.08, 130.63, 129.84, 129.71, 129.61, 128.99, 120.46, 117.21, 110.89, 101.50, 76.08, 73.80, 70.77, 68.60, 60.82. HRMS  $[\text{M} + \text{Na}]^+$  calculated for  $\text{C}_{16}\text{H}_{17}\text{BrO}_6\text{Na}^+$  407.0101, found 407.0109.



**Figure S1.** <sup>1</sup>H NMR spectrum of BrNP-Gla in DMSO-*d*<sub>6</sub>.



**Figure S2.** <sup>13</sup>C NMR spectrum of BrNP-Gla in DMSO-*d*<sub>6</sub>.

Multiple Mass Analysis: 2 mass(es) processed  
 Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0  
 Element prediction: Off  
 Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions  
 378 formula(e) evaluated with 2 results within limits (up to 50 best isotopic matches for each mass)  
 Elements Used:  
 C: 16-16 H: 0-32 O: 0-6 Na: 0-1 79Br: 0-4 81Br: 0-4

ZOU-L  
 ZL-YZY-181 64 (1.618) Cm (61.64)

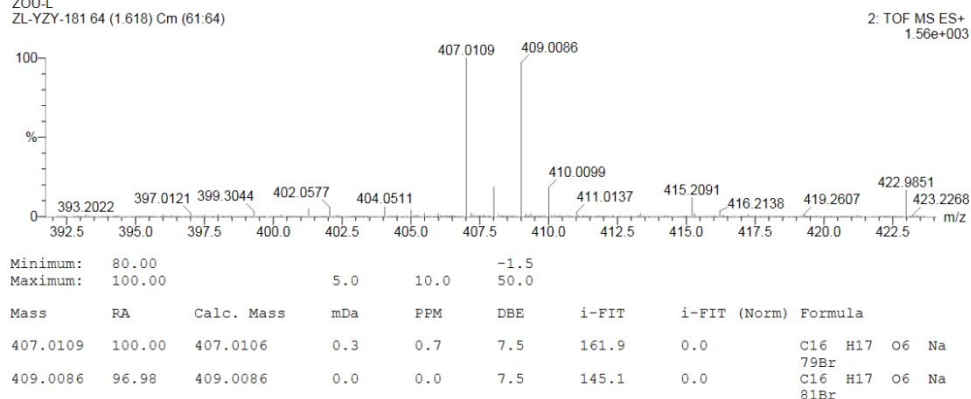
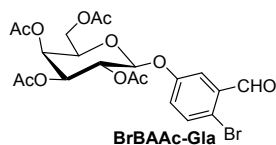
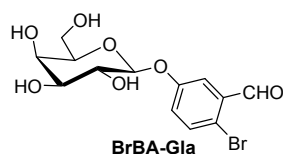


Figure S3. ESI high-resolution mass spectrum of BrNP-Gla.



Scheme S4. Chemical structure of BrBAAc-Gla

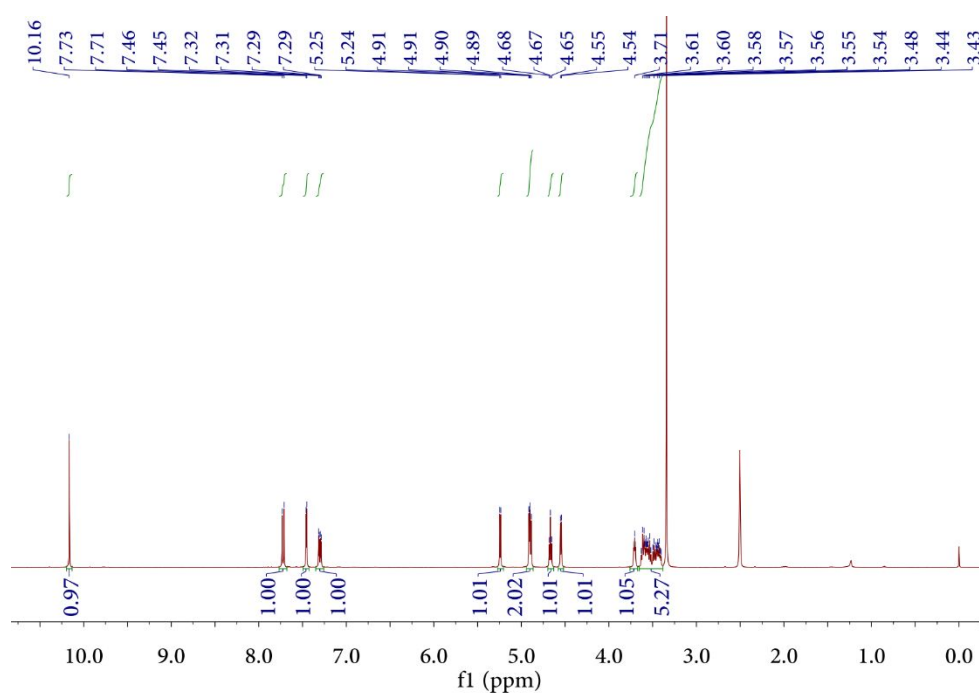
BrBAAc-Gla  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.31 (s, 1H), 7.63 – 7.50 (m, 2H), 7.13 (dd,  $J$  = 8.7, 3.1 Hz, 1H), 5.57 – 5.45 (m, 2H), 5.21 – 5.04 (m, 2H), 4.29 – 4.02 (m, 3H), 2.19 (s, 3H), 2.11 (s, 3H), 2.08 (s, 3H), 2.02 (s, 3H).



Scheme S5. Chemical structure of BrBA-Gla

BrBA-Gla  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  10.16 (s, 1H), 7.72 (d,  $J$  = 8.8 Hz, 1H), 7.46 (d,  $J$  = 3.1 Hz, 1H), 7.30 (dd,  $J$  = 8.8, 3.1 Hz, 1H), 5.24 (d,  $J$  = 5.1 Hz,

1H), 4.90 (dd,  $J = 6.7, 4.0$  Hz, 2H), 4.67 (t,  $J = 5.5$  Hz, 1H), 4.55 (d,  $J = 4.6$  Hz, 1H), 3.71 (s, 1H), 3.65 – 3.38 (m, 5H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{DMSO}-d_6$ )  $\delta$  191.36, 157.12, 134.86, 133.74, 124.20, 117.32, 116.94, 101.14, 75.56, 73.02, 70.13, 67.94, 60.14. HRMS  $[\text{M} + \text{Na}]^+$  calculated for  $\text{C}_{13}\text{H}_{15}\text{BrO}_7\text{Na}^+$  384.9893, found 384.9895



**Figure S4.**  $^1\text{H}$  NMR spectrum of BrBA-Gla in  $\text{DMSO}-d_6$ .

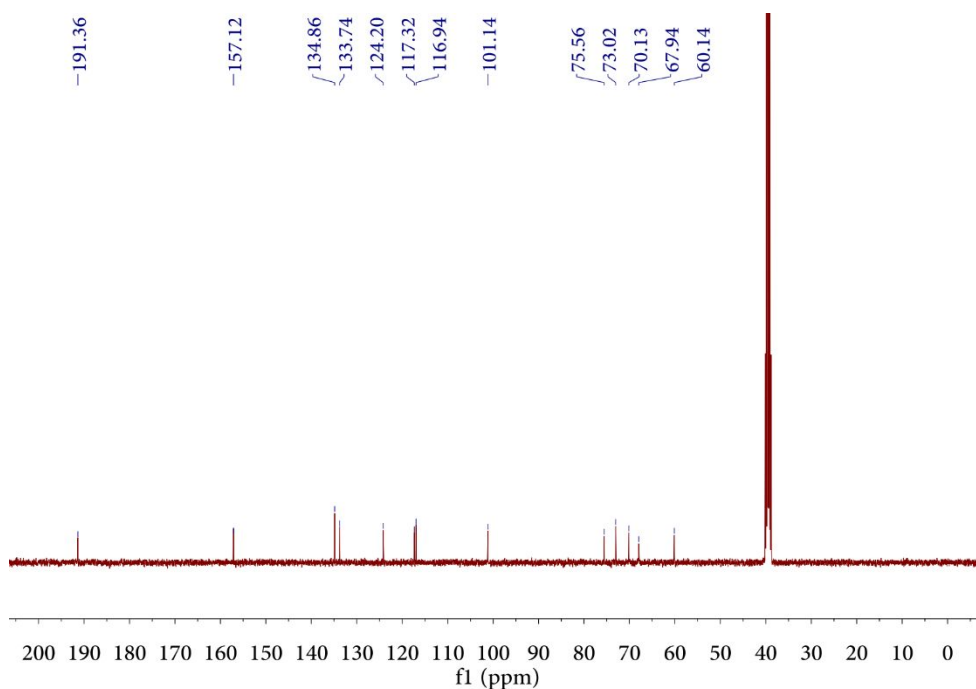


Figure S5.  $^{13}\text{C}$  NMR spectrum of BrBA-Gla in  $\text{DMSO}-d_6$ .

#### Elemental Composition Report

Page 1

#### Multiple Mass Analysis: 2 mass(es) processed

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

390 formula(e) evaluated with 2 results within limits (up to 50 best isotopic matches for each mass)

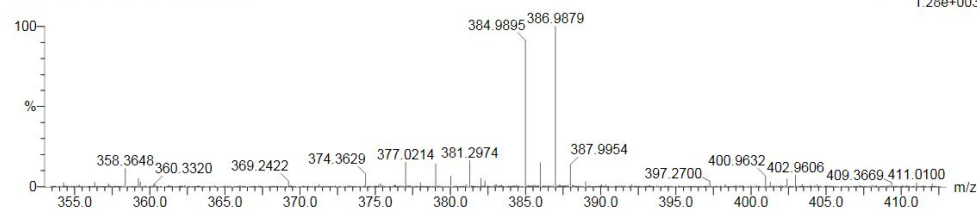
Elements Used:

C: 13-13 H: 0-32 O: 0-7 Na: 0-1  $^{79}\text{Br}$ : 0-4  $^{81}\text{Br}$ : 0-4

ZOU-L

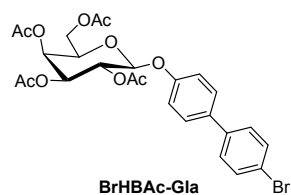
ZL-YZY-183 119 (3.013) Cm (114.120)

2: TOF MS ES+  
1.28e+003



Minimum:	80.00				-1.5				
Maximum:	100.00		5.0	10.0	50.0				
Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula	
384.9895	91.16	384.9899	-0.4	-1.0	5.5	176.6	0.0	C13 H15 O7 Na	$^{79}\text{Br}$
386.9879	100.00	386.9878	0.1	0.3	5.5	142.8	0.0	C13 H15 O7 Na	$^{81}\text{Br}$

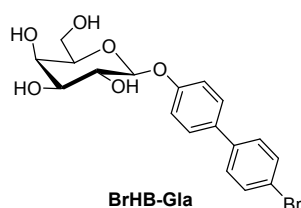
Figure S6. ESI high-resolution mass spectrum of BrBA-Gla.





**Scheme S6.** Chemical structure of BrHBAC-Gla

**BrHBAC-Gla**  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  7.73 – 7.56 (m, 6H), 7.12 – 7.05 (m, 2H), 5.53 (d,  $J$  = 7.7 Hz, 1H), 5.40 – 5.19 (m, 3H), 4.47 (t,  $J$  = 6.4 Hz, 1H), 4.11 (dd,  $J$  = 6.3, 2.3 Hz, 2H), 2.16 (s, 3H), 2.06 (s, 3H), 2.03 (s, 3H), 1.96 (s, 3H).



**Scheme S7.** Chemical structure of BrHB-Gla

**BrHB-Gla**  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  7.65 – 7.55 (m, 6H), 7.17 – 7.08 (m, 2H), 5.21 (d,  $J$  = 5.1 Hz, 1H), 4.89 (dd,  $J$  = 9.2, 6.6 Hz, 2H), 4.69 (t,  $J$  = 5.3 Hz, 1H), 4.54 (d,  $J$  = 4.7 Hz, 1H), 3.72 (s, 1H), 3.64 – 3.46 (m, 4H), 3.43 (ddd,  $J$  = 9.2, 5.7, 3.3 Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{DMSO}-d_6$ )  $\delta$  157.39, 138.90, 132.25, 131.69, 128.32, 127.58, 120.17, 116.72, 100.92, 75.51, 73.23, 70.22, 68.09, 60.33. HRMS  $[\text{M} + \text{Na}]^+$  calculated for  $\text{C}_{18}\text{H}_{19}\text{BrO}_6\text{Na}^+$  435.0237, found 435.0237

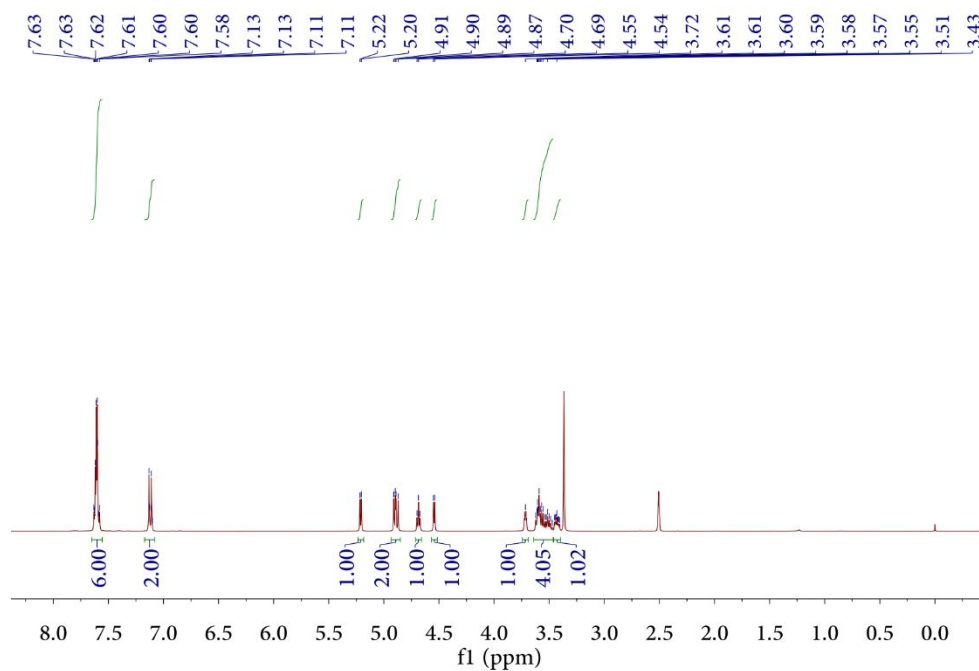


Figure S7.  $^1\text{H}$  NMR spectrum of BrHB-Gla in  $\text{DMSO}-d_6$ .

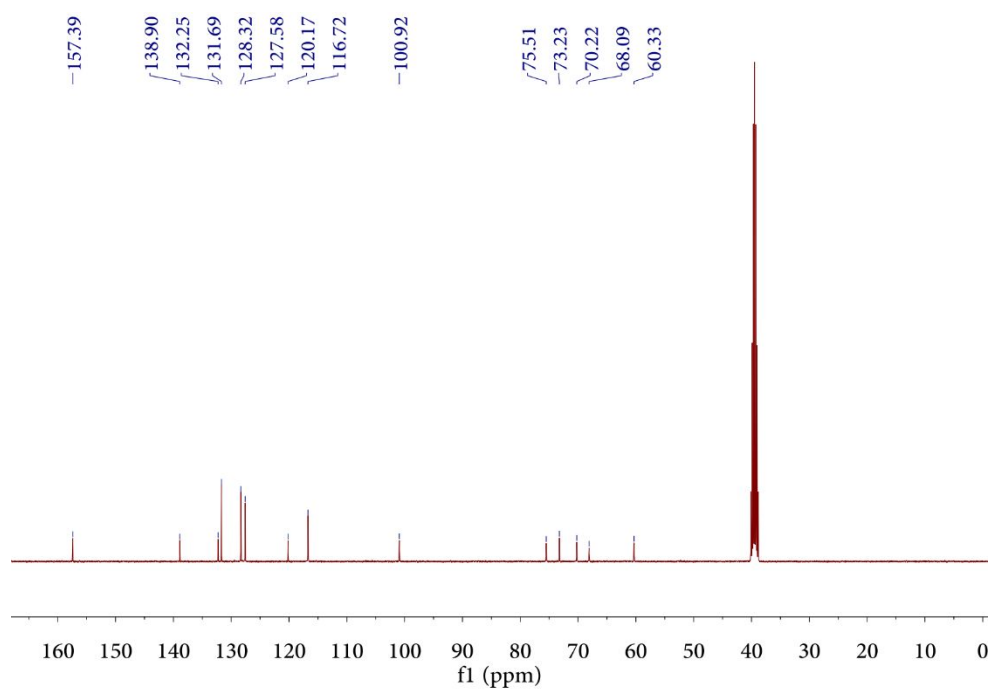


Figure S8.  $^{13}\text{C}$  NMR spectrum of BrHB-Gla in  $\text{DMSO}-d_6$ .

**Multiple Mass Analysis: 2 mass(es) processed**

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

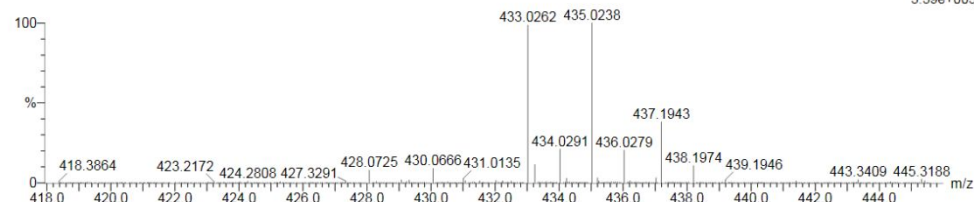
420 formula(e) evaluated with 2 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

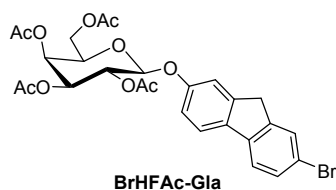
C: 18-18 H: 0-32 O: 0-6 Na: 0-1 79Br: 0-4 81Br: 0-4

ZOU-L

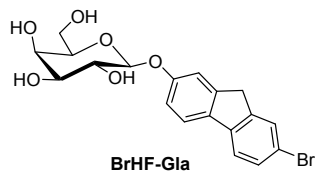
ZL-YZY-182 77 (1.961) Cm (77.88)

2: TOF MS ES+  
3.39e+003

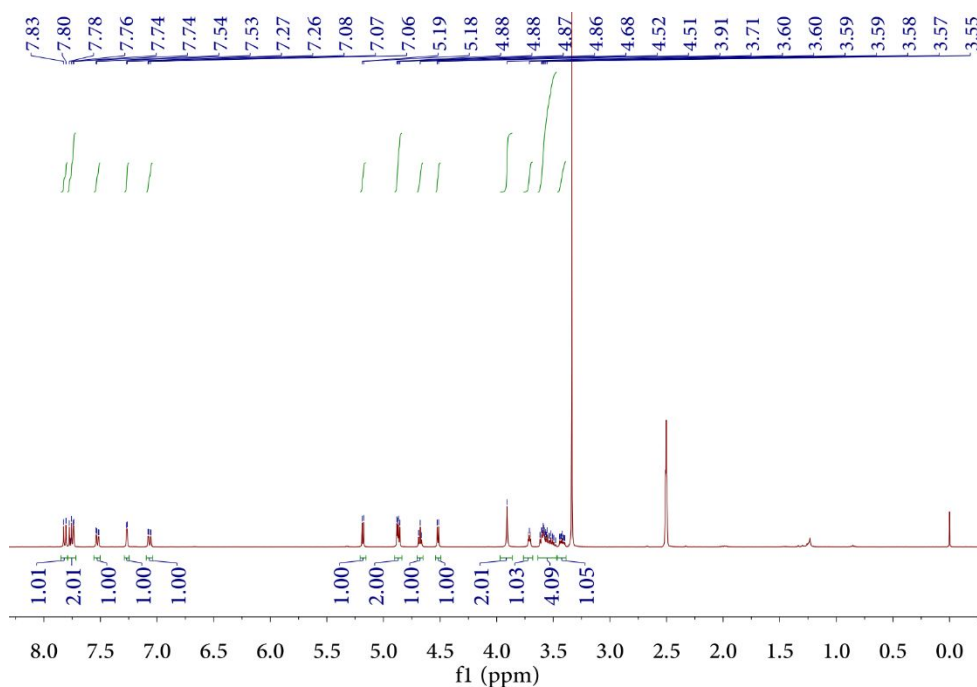
Minimum:	80.00				-1.5				
Maximum:	100.00		5.0	10.0	50.0				
Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula	
433.0262	98.67	433.0263	-0.1	-0.2	8.5	239.5	0.0	C18 H19 O6 Na	79Br
435.0238	100.00	435.0242	-0.4	-0.9	8.5	224.5	0.0	C18 H19 O6 Na	81Br

**Figure S9.** ESI high-resolution mass spectrum of BrHB-Gla**Scheme S8.** Chemical structure of BrHFAc-Gla

**BrHFAc-Gla**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , roughly)  $\delta$  7.68 – 7.63 (m, 2H), 7.57 (d,  $J$  = 8.1 Hz, 1H), 7.48 (dd,  $J$  = 8.1, 1.8 Hz, 1H), 7.19 (d,  $J$  = 2.2 Hz, 1H), 7.03 (dd,  $J$  = 8.3, 2.3 Hz, 1H), 5.56 – 5.45 (m, 2H), 5.13 (dd,  $J$  = 10.5, 3.4 Hz, 1H), 5.10 – 5.04 (m, 1H), 4.20 – 4.01 (m, 3H), 3.86 (s, 2H), 2.20 (s, 3H), 2.09 (s, 3H), 2.08 (s, 3H), 2.03 (s, 3H).

**Scheme S9.** Chemical structure of BrHF-Gla

BrHF-Gla  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  7.81 (d,  $J$  = 8.4 Hz, 1H), 7.79 – 7.71 (m, 2H), 7.53 (dd,  $J$  = 8.0, 1.9 Hz, 1H), 7.27 (d,  $J$  = 2.3 Hz, 1H), 7.07 (dd,  $J$  = 8.4, 2.3 Hz, 1H), 5.18 (d,  $J$  = 5.2 Hz, 1H), 4.87 (dd,  $J$  = 6.6, 3.6 Hz, 2H), 4.68 (t,  $J$  = 5.3 Hz, 1H), 4.52 (d,  $J$  = 4.7 Hz, 1H), 3.91 (s, 2H), 3.71 (s, 1H), 3.65 – 3.47 (m, 4H), 3.42 (ddd,  $J$  = 9.3, 5.7, 3.3 Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz, DMSO)  $\delta$  158.01, 145.70, 145.03, 140.80, 134.41, 130.02, 128.46, 121.57, 121.45, 119.14, 116.06, 113.64, 101.87, 76.02, 73.75, 70.80, 68.61, 60.84, 36.95. HRMS  $[\text{M} + \text{Na}]^+$  calculated for  $\text{C}_{19}\text{H}_{19}\text{BrO}_6\text{Na}^+$  447.0237, found 447.0239.



**Figure S10.**  $^1\text{H}$  NMR spectrum of BrHF-Gla in  $\text{DMSO}-d_6$ .

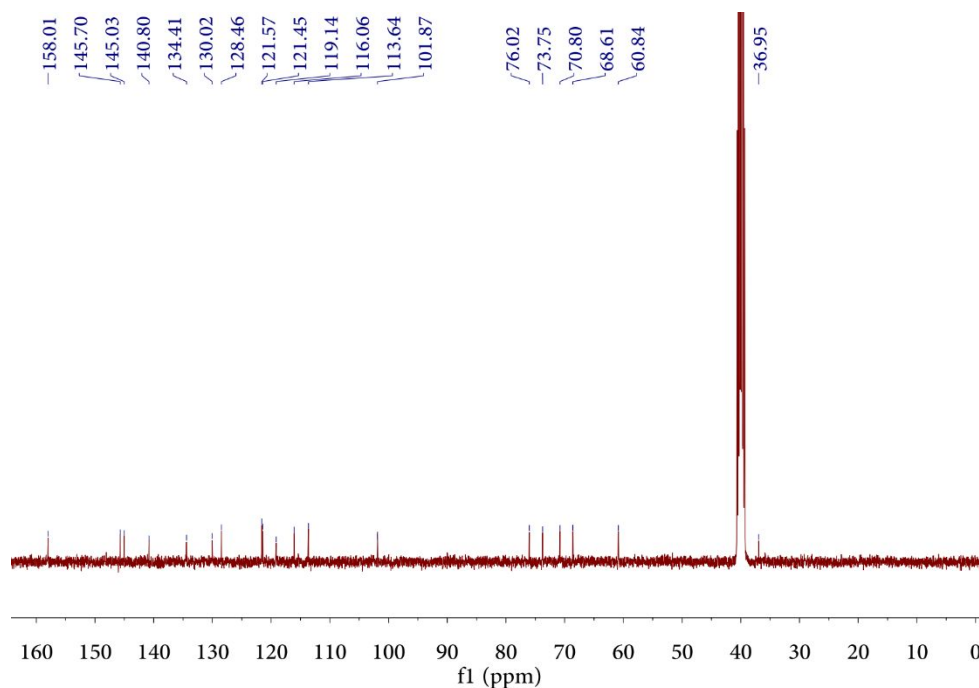


Figure S11.  $^{13}\text{C}$  NMR spectrum of BrHF-Gla in  $\text{DMSO-}d_6$ .

#### Elemental Composition Report

Page 1

#### Multiple Mass Analysis: 2 mass(es) processed

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

491 formula(e) evaluated with 2 results within limits (up to 50 best isotopic matches for each mass)

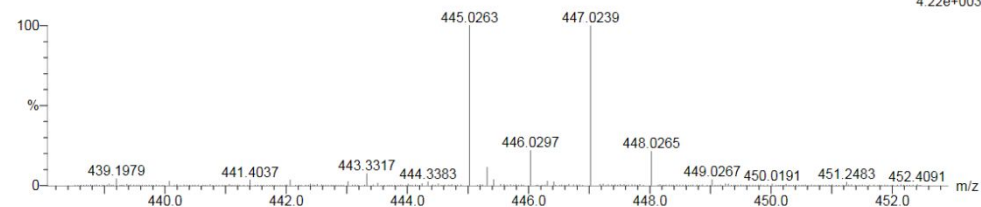
Elements Used:

C: 19-19 H: 0-32 O: 0-7 Na: 0-1  $^{79}\text{Br}$ : 0-4  $^{81}\text{Br}$ : 0-4

ZOU-L

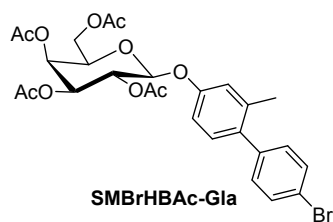
ZL-YZY-184 21 (0.546) Cm (21:33)

2: TOF MS ES+  
4.22e+003



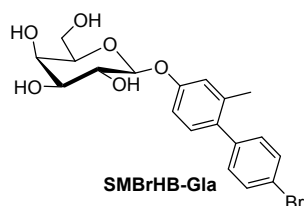
Minimum:	80.00				-1.5				
Maximum:	100.00				50.0				
Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula	
445.0263	100.00	445.0263	0.0	0.0	9.5	252.6	0.0	C19 H19 O6 Na	
447.0239	99.88	447.0242	-0.3	-0.7	9.5	253.5	0.0	$^{79}\text{Br}$	
								C19 H19 O6 Na	
								$^{81}\text{Br}$	

Figure S12. ESI high-resolution mass spectrum of BrHF-Gla.



**Scheme S10.** Chemical structure of SBrHB-Ac-Gla.

**SBrHB-Ac-Gla**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , roughly)  $\delta$  7.60 – 7.46 (m, 2H), 7.18 – 7.13 (m, 2H), 7.12 (d,  $J$  = 8.3 Hz, 1H), 6.91 (d,  $J$  = 2.6 Hz, 1H), 6.87 (dd,  $J$  = 8.3, 2.7 Hz, 1H), 5.55 – 5.46 (m, 2H), 5.13 (dd,  $J$  = 10.5, 3.5 Hz, 1H), 5.10 – 5.06 (m, 1H), 4.27 – 3.93 (m, 3H), 2.23 (s, 3H), 2.20 (s, 3H), 2.09 (s, 3H), 2.07 (s, 3H), 2.03 (s, 3H).



**Scheme S11.** Chemical structure of SBrHB-Gla.

**SBrHB-Gla**  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  7.65 – 7.56 (m, 2H), 7.31 – 7.24 (m, 2H), 7.11 (d,  $J$  = 8.3 Hz, 1H), 6.97 (d,  $J$  = 2.5 Hz, 1H), 6.93 (dd,  $J$  = 8.3, 2.7 Hz, 1H), 5.16 (d,  $J$  = 5.2 Hz, 1H), 4.90 – 4.80 (m, 2H), 4.69 – 4.62 (m, 1H), 4.51 (d,  $J$  = 4.6 Hz, 1H), 3.70 (t,  $J$  = 4.1 Hz, 1H), 3.63 – 3.45 (m, 4H), 3.41 (ddd,  $J$  = 9.3, 5.8, 3.3 Hz, 1H), 2.20 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz, **DMSO**)  $\delta$  157.42, 140.62, 136.44, 134.07, 131.78, 131.55, 130.84, 120.51, 118.66, 114.32, 101.53, 75.97, 73.77, 70.74, 68.59, 60.82, 20.86. HRMS  $[\text{M} + \text{Na}]^+$  calculated for  $\text{C}_{19}\text{H}_{21}\text{BrO}_6\text{Na}^+$  447.0414, found 447.0421.

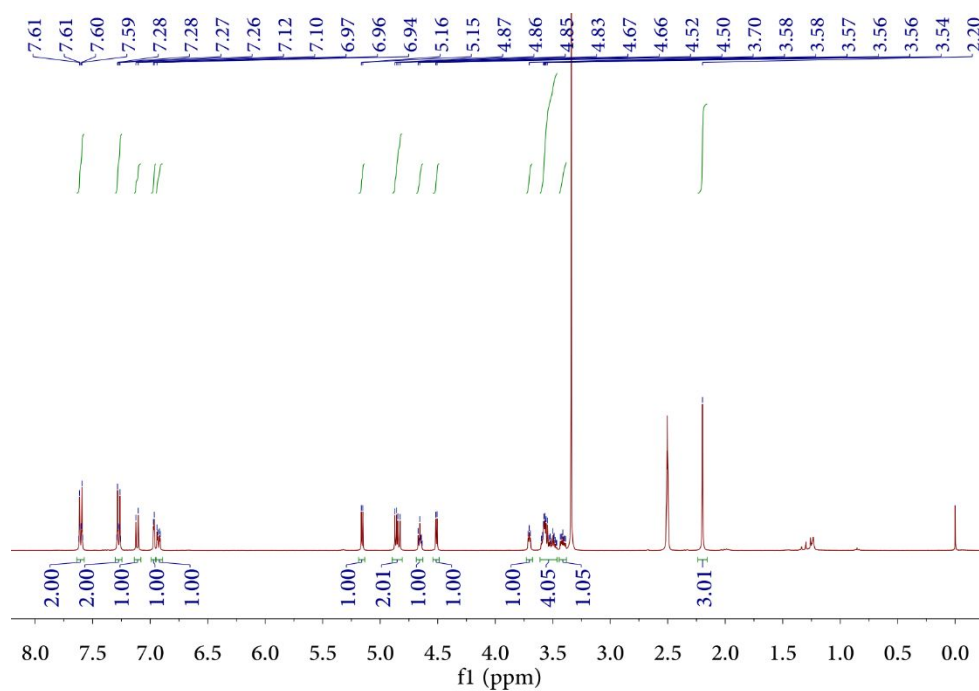


Figure S13. <sup>1</sup>H NMR spectrum of SBrHB-Gla in DMSO-*d*<sub>6</sub>.

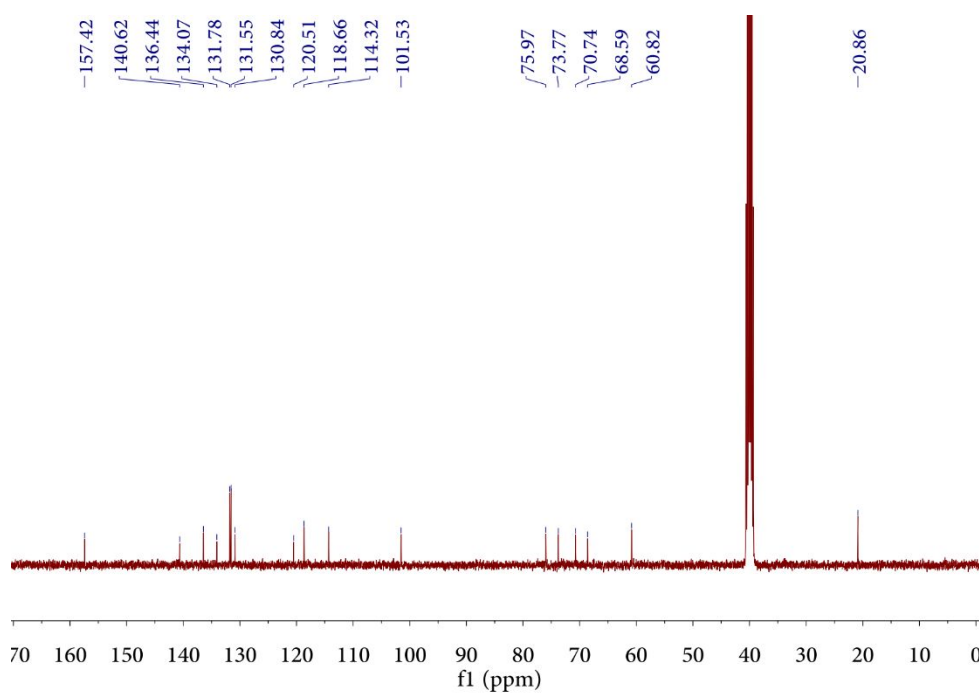


Figure S14. <sup>13</sup>C NMR spectrum of SBrHB-Gla in DMSO-*d*<sub>6</sub>.

## Single Mass Analysis

Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

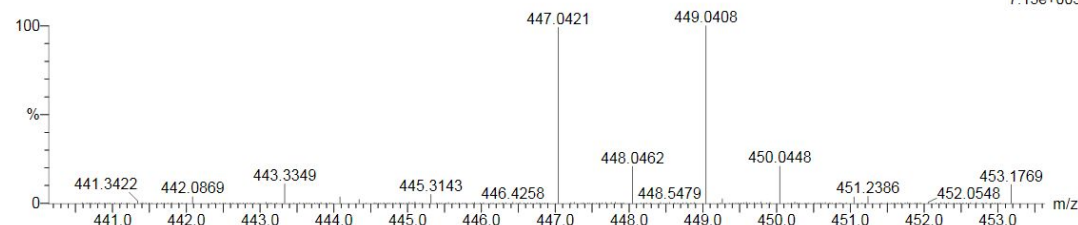
54 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

C: 0-19 H: 0-54 O: 0-9 Na: 0-1 Br: 0-1

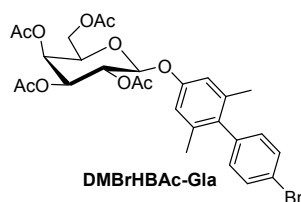
ZOU-L

ZL-YZY-185 14 (0.365) Cm (12:18)

2: TOF MS ES+  
7.15e+003

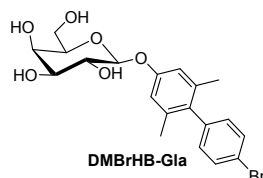
Minimum:				-1.5				
Maximum:		5.0	20.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula	
447.0421	447.0419	0.2	0.4	8.5	195.3	0.0	C19	H21 O6 Na Br

Figure S15. ESI high-resolution mass spectrum of SBrHB-Gla.



Scheme S12. Chemical structure of DMBrHB-Gla.

DMBrHB-Gla  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.61 – 7.48 (m, 2H), 7.07 – 6.94 (m, 2H), 6.75 (s, 2H), 5.56 – 5.45 (m, 2H), 5.17 – 5.04 (m, 2H), 4.31 – 4.02 (m, 3H), 2.19 (s, 3H), 2.09 (s, 3H), 2.06 (d, 3H), 2.02 (s, 3H), 2.00 (s, 6H).

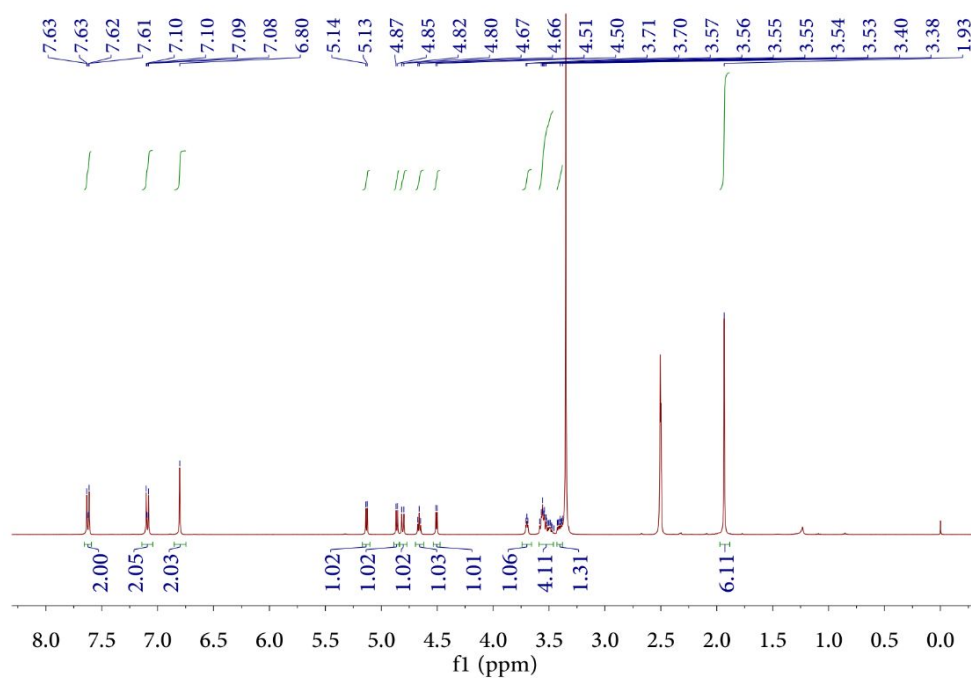


Scheme S13. Chemical structure of DMBrHB-Gla.

DMBrHB-Gla  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ )  $\delta$  7.66 – 7.59 (m, 2H), 7.14 – 7.04 (m, 2H), 6.80 (s, 2H), 5.13 (d,  $J$  = 5.2 Hz, 1H), 4.86 (d,  $J$  = 5.7 Hz, 1H),



4.81 (d,  $J = 7.7$  Hz, 1H), 4.66 (t,  $J = 5.3$  Hz, 1H), 4.51 (d,  $J = 4.6$  Hz, 1H), 3.74 – 3.66 (m, 1H), 3.61 – 3.45 (m, 4H), 3.44 – 3.37 (m, 1H), 1.93 (s, 6H).  $^{13}\text{C}$  NMR (151 MHz, DMSO)  $\delta$  156.97, 139.94, 136.85, 134.22, 132.17, 131.91, 120.50, 115.70, 101.62, 75.97, 73.82, 70.80, 68.62, 60.85, 21.23. HRMS  $[\text{M} + \text{Na}]^+$  calculated for  $\text{C}_{20}\text{H}_{23}\text{BrO}_6\text{Na}^+$  463.0550, found 461.0551.



**Figure S16.**  $^1\text{H}$  NMR spectrum of DMBrHB-Gla in  $\text{DMSO}-d_6$ .

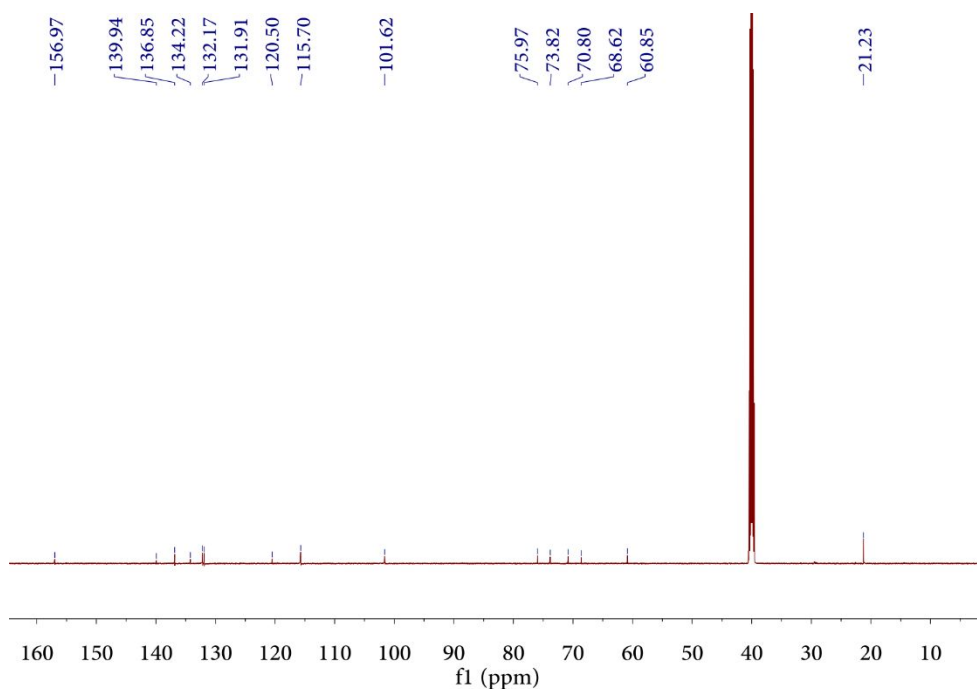


Figure S17.  $^{13}\text{C}$  NMR spectrum of DMBrHB-Gla in  $\text{DMSO}-d_6$ .

#### Elemental Composition Report

Page 1

#### Multiple Mass Analysis: 2 mass(es) processed

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

625 formula(e) evaluated with 2 results within limits (up to 50 best isotopic matches for each mass)

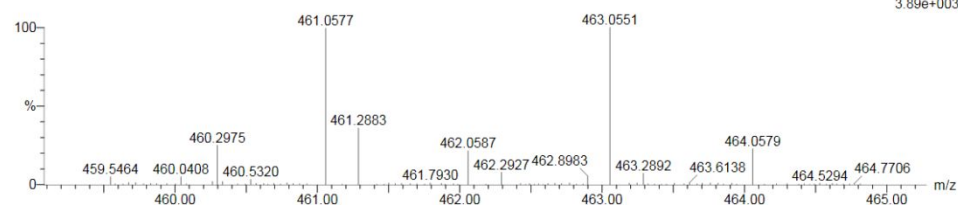
Elements Used:

C: 20-20 H: 0-54 O: 0-9 Na: 0-1 79Br: 0-4 81Br: 0-4

ZOU-L

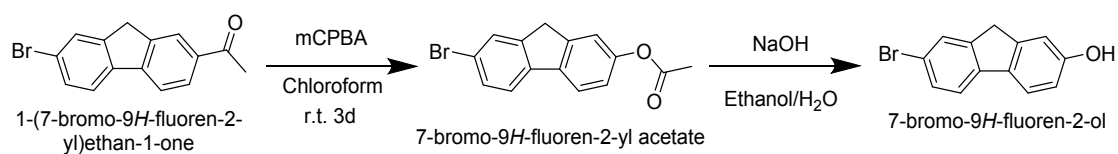
ZL-YZY-186 13 (0.344) Cm (13.29)

2: TOF MS ES+  
3.89e+003



Minimum:	80.00				-1.5				
Maximum:	100.00		5.0	10.0	50.0				
Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula	
461.0577	99.43	461.0576	0.1	0.2	8.5	253.0	0.0	C20 H23 O6 Na	
463.0551	100.00	463.0555	-0.4	-0.9	8.5	199.3	0.0	79Br C20 H23 O6 Na	81Br

Figure S18. ESI high-resolution mass spectrum of SMBrHB-Gla

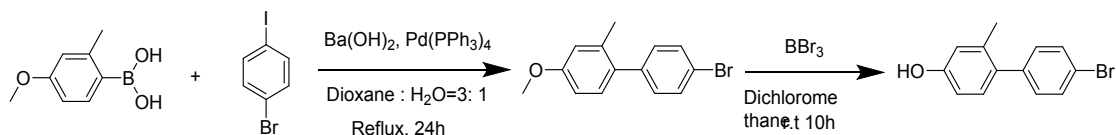


#### **Scheme S14** General synthesis of 7-bromo-9H-fluoren-2-ol

**Synthesis of 7-bromo-9H-fluoren-2-yl acetate** To a 100 mL three-necked flask, 1-(7-bromo-9H-fluoren-2-yl)ethan-1-one (2.86 g, 1 e.q.) was dissolved in 60 mL chloroform, the solution was cooled with an ice water and kept in darkness. 3-chloroperbenzoic acid (mCPBA, 1.9 g, 1.1 e.q.) was added slowly in portions. The mixture was stirred at 0°C for another 8h and then stirred at room temperature for 3 days. The reaction was quenched with a saturated NaHCO<sub>3</sub> aqueous solution and extracted with dichloromethane. The collected organic phase was evaporated to obtain the crude product, which was further purified by column chromatography (PE: DCM= 4:1) to yield as a white powder (80%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.72 (d, *J* = 8.2 Hz, 1H), 7.66 (d, *J* = 1.6 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.49 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.26 (d, *J* = 1.9 Hz, 1H), 7.09 (dd, *J* = 8.3, 2.2 Hz, 1H), 3.88 (s, 2H), 2.33 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 169.82, 150.01, 145.22, 144.25, 139.94, 138.57, 130.05, 128.26, 121.08, 120.54, 120.50, 120.48, 118.62, 36.77, (21.23, 21.20).

**Synthesis of 7-bromo-9H-fluoren-2-ol** 7-bromo-9H-fluoren-2-yl acetate was suspended in 100 mL ethanol, an excess aqueous solution of NaOH was added carefully, the reaction was monitored by TLC, at the end of the reaction, 1M diluted hydrochloric acid was added to neutralize the solution. After evaporating the solvent, the mixture was suspended in water and extracted with dichloromethane. The organic layer was gathered and further purified with

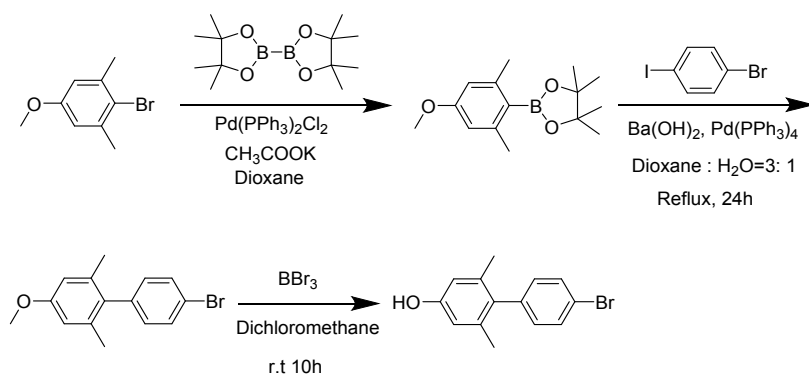
column chromatography (DCM) to yield the product as a white powder.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66 – 7.54 (m, 2H), 7.52 (d,  $J$  = 8.1 Hz, 1H), 7.46 (dd,  $J$  = 8.1, 1.8 Hz, 1H), 7.01 (d,  $J$  = 2.4 Hz, 1H), 6.85 (dd,  $J$  = 8.2, 2.4 Hz, 1H), 3.83 (s, 2H).



### Scheme S15 Synthesis of 4'-bromo-2-methyl-[1,1'-biphenyl]-4-ol

**Synthesis of 4'-bromo-4-methoxy-2-methyl-1,1'-biphenyl** 4-methoxy-2-methylphenyl)boronic acid (1 e.q.) and 1-bromo-4-iodobenzene (1.5 e.q.) was dissolved in 50 mL water dioxane mixture (water: dioxane= 1:3), the solution was degassed with  $\text{N}_2$  for 10 min, tetrakis(triphenylphosphine)palladium (0.05 e.q.) and  $\text{Ba}(\text{OH})_2$  (5 e.q.) was then added, the reaction was heated to reflux and further stirred for 30 hours. The mixture was filtrated to collect the filtrate, and neutralized with hydrochloric acid. The product was extracted with dichloromethane and further purified with column chromatography (first: PE, second: PE: DCM= 3:1) to yield the product as a colourless oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54 – 7.48 (m, 1H), 7.19 – 7.14 (m, 1H), 7.11 (d,  $J$  = 8.3 Hz, 0H), 6.81 (d,  $J$  = 2.7 Hz, 1H), 6.78 (dd,  $J$  = 8.3, 2.8 Hz, 1H), 3.82 (s, 2H), 2.24 (s, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.02, 140.58, 136.67, 133.32, 131.22, 131.15, 130.72, 120.68, 115.88, 111.28, (55.31, 55.28), (20.79, 20.76).

**Synthesis of 4'-bromo-2-methyl-[1,1'-biphenyl]-4-ol** 4'-bromo-4-methoxy-2-methyl-1,1'-biphenyl was dissolved in dichloromethane and stirred at 0 °C for 10 min, then a dichloromethane solution of boron tribromide (3 e.q.) was added carefully. The reaction was stirred at 0 °C for another 1 hour and then stirred at room temperature for 3 hours. The reaction was quenched with 200 mL ice water and extracted with dichloromethane. The organic layer was collected and purified with column chromatography (PE: DCM= 3:2) to yield the product as white crystals. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.56 – 7.47 (m, 2H), 7.20 – 7.10 (m, 2H), 7.07 (d, *J* = 8.2 Hz, 1H), 6.75 (d, *J* = 2.8 Hz, 1H), 6.71 (dd, *J* = 8.3, 2.7 Hz, 1H), 2.21 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 154.84, 140.43, 137.01, 133.53, 131.21, 131.11, 130.93, 120.70, 117.08, 112.82, (20.56, 20.55).



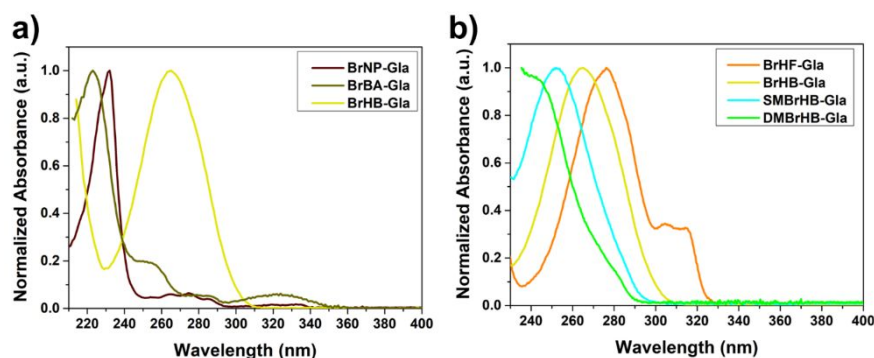
**Scheme S16** Synthesis of 4'-bromo-4-methoxy-2,6-dimethyl-1,1'-biphenyl and 4'-bromo-2,6-dimethyl-[1,1'-biphenyl]-4-ol

**Synthesis of 4-Methoxybenzeneboronic acid, pinacol ester** 2-bromo-5-methoxy-1,3-dimethylbenzene and bis(pinacolato)diboron was dissolved in dioxane, the solution was degassed with N<sub>2</sub> for 10 min, Trans-

dichlorobis(triphenyl-phosphine)palladium(II) (0.05 e.q.) and potassium acetate were added, and the mixture was heated to reflux and stirred overnight. The reaction mixture was suspended in dichloromethane and filtrated over a thin silica powder, the organic solvent of the filtrate was evaporated and purified with column chromatography to yield as a white crystal.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.51 (s, 2H), 3.76 (s, 3H), 2.39 (s, 6H), 1.37 (s, 12H).

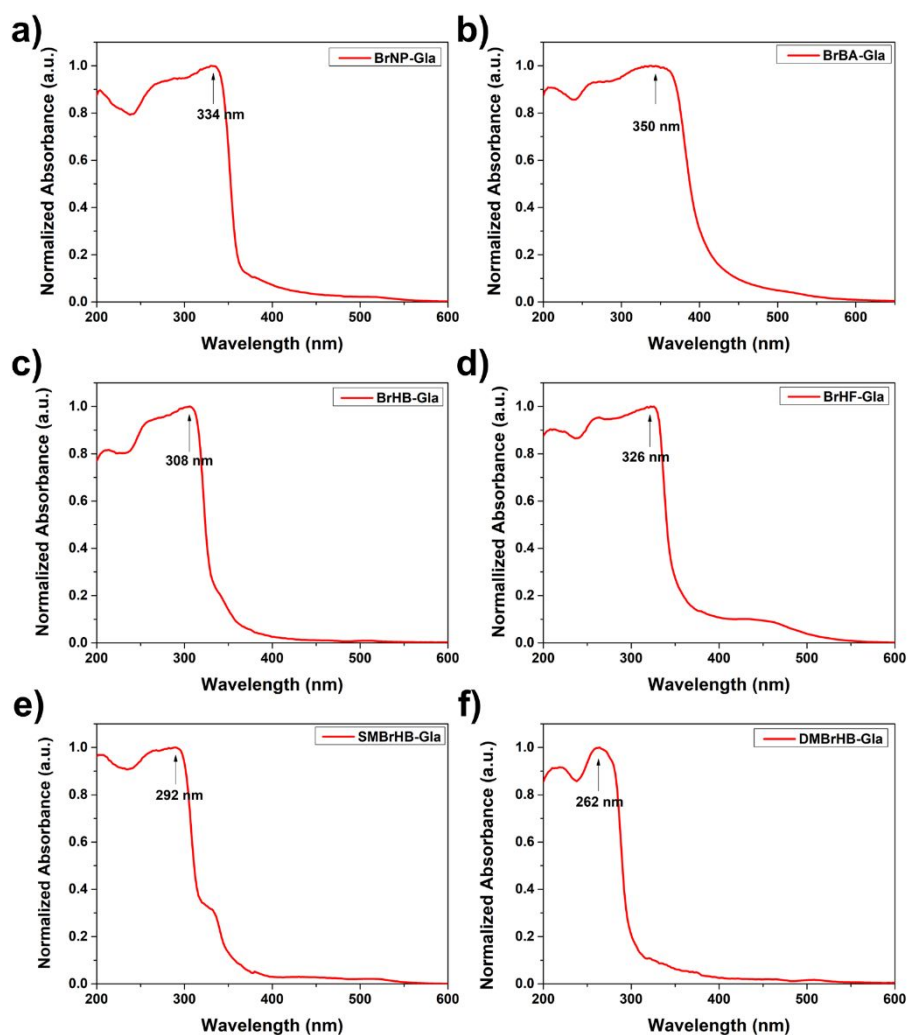
**Synthesis of 4'-bromo-4-methoxy-2,6-dimethyl-1,1'-biphenyl and 4'-bromo-2,6-dimethyl-[1,1'-biphenyl]-4-ol** The synthesis methods of these two compounds are the same to the synthesis of 4'-bromo-4-methoxy-2-methyl-1,1'-biphenyl and 4'-bromo-2-methyl-[1,1'-biphenyl]-4-ol above.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58 – 7.50 (m, 2H), 7.03 – 6.96 (m, 2H), 6.59 (s, 2H), 1.97 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  154.36, 139.65, 137.67, 133.35, 131.59, 131.47, 120.66, 114.04, 20.92.

## Result and Discussion

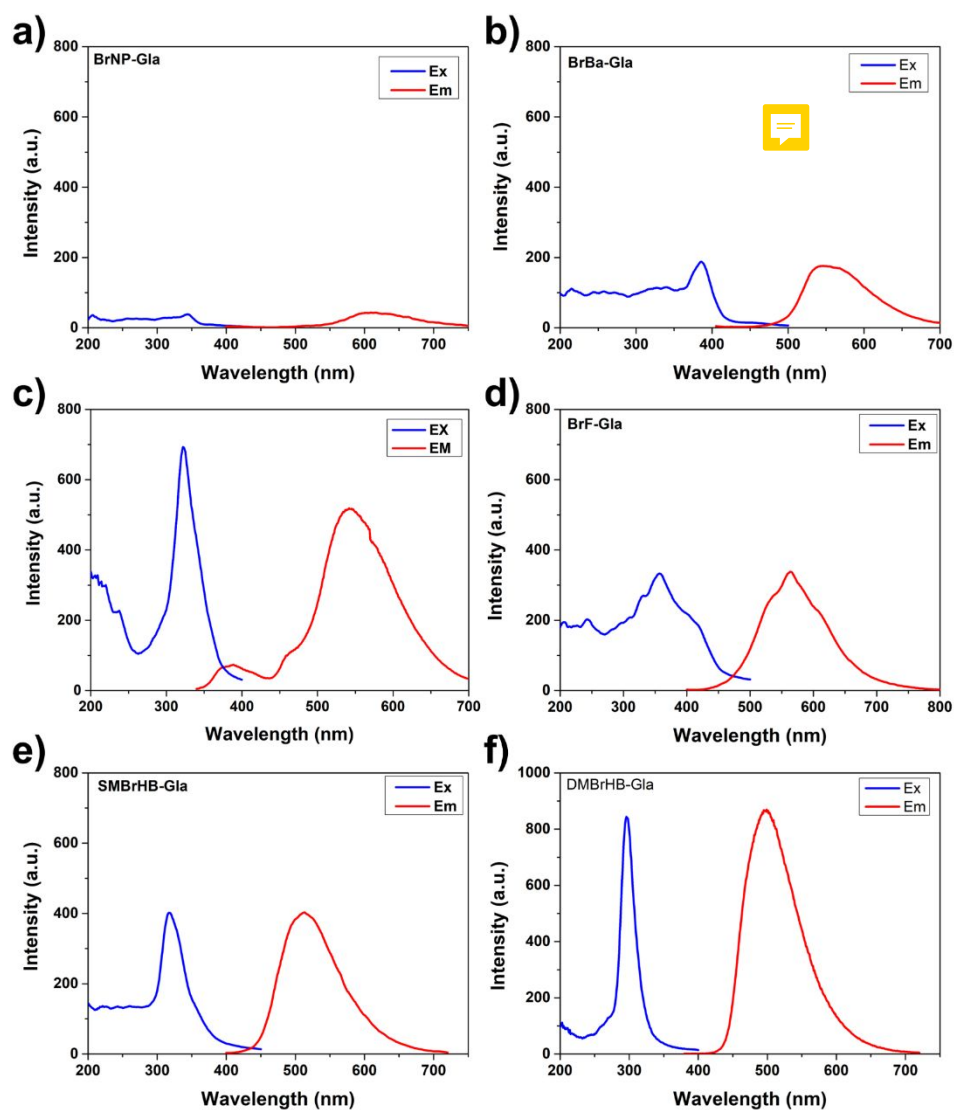


**Figure S19.** Normalized absorption spectrum of a) BrNP-Gla ( $1 \times 10^{-5}$  M), BrBA-Gla ( $2 \times 10^{-5}$  M), and BrHB-Gla ( $2 \times 10^{-5}$  M) in methanol b) BrHF-Gla ( $2 \times 10^{-5}$  M), BrHB-Gla ( $2 \times 10^{-5}$  M), SMBrHB-Gla ( $2 \times 10^{-5}$  M), and DMBrHB-Gla ( $2 \times 10^{-5}$  M) in methanol

M), BrHB-Gla ( $2 \times 10^{-5}$  M), SBrHB-Gla ( $2 \times 10^{-5}$  M), DMBBrHB-Gla ( $2 \times 10^{-5}$  M) in methanol.

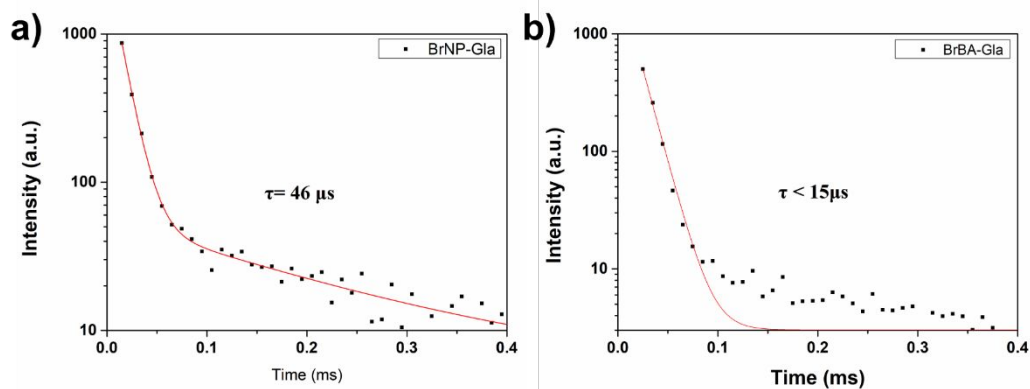


**Figure S20.** The absorption spectra of a) BrNP-Gla, b) BrBA-Gla, c) BrHB-Gla, d) BrHF-Gla, e) SBrHB-Gla, f) DMBBrHB-Gla in the amorphous solid state.

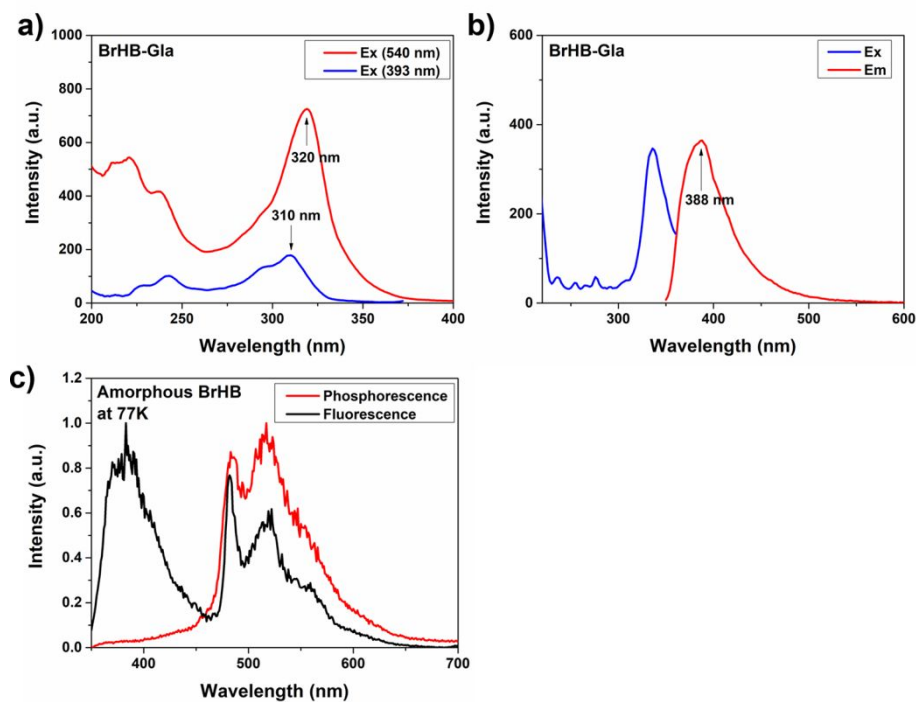


**Figure S21.** RTP excitation and emission spectra of a) BrNP-Gla,  $\lambda_{em}$ = 605 nm,  $\lambda_{ex}$ = 337 nm; b) BrBA-Gla,  $\lambda_{em}$ = 545 nm,  $\lambda_{ex}$ = 386 nm; c) BrHB-Gla,  $\lambda_{em}$ = 540 nm,  $\lambda_{ex}$ = 320 nm; d) BrHF-Gla,  $\lambda_{em}$ = 562 nm,  $\lambda_{ex}$ = 362 nm; e) SBrHB-Gla,  $\lambda_{em}$ = 512 nm,  $\lambda_{ex}$ = 318 nm; f) DMBRHB-Gla,  $\lambda_{em}$ = 493 nm,  $\lambda_{ex}$ = 296 nm, in amorphous solid state.

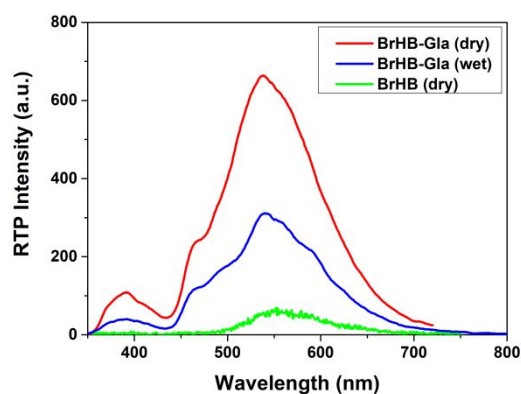




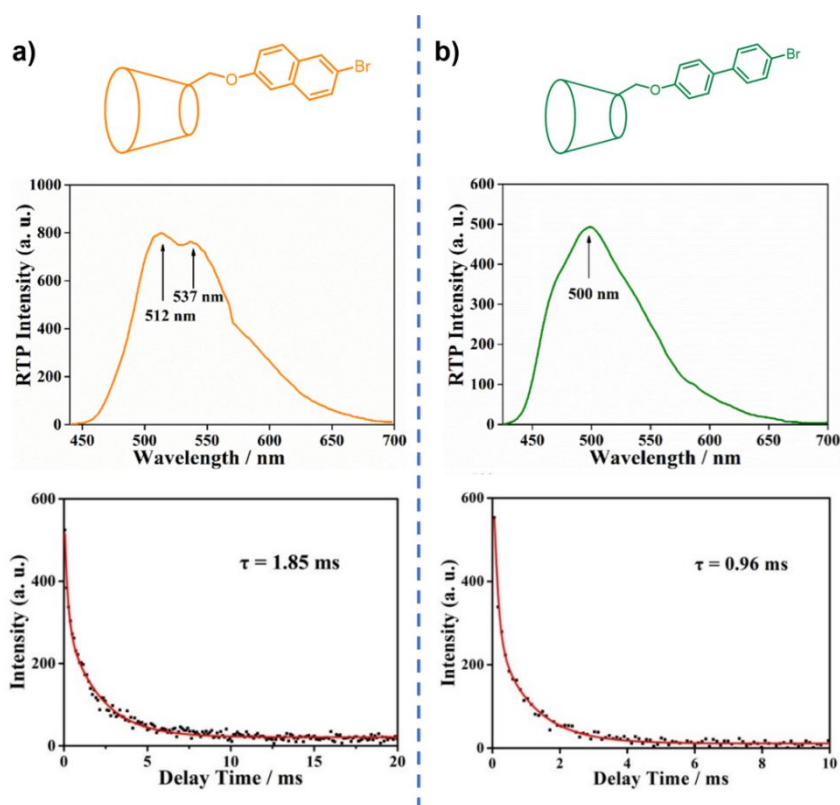
**Figure S22.** PL Emission lifetime of a) BrNP-Gla at 605 nm,  $\lambda_{ex} = 337$  nm; b) BrBA-Gla at 545 nm,  $\lambda_{ex} = 386$  nm.



**Figure S23.** a) RTP excitation spectra of amorphous BrHB-Gla at the wavelength of 540 nm and 393 nm; b) Fluorescence emission and excitation spectra of amorphous BrHB-Gla; c) Phosphorescence and Fluorescence emission spectra of amorphous BrHB-Gla at 77K,  $\lambda_{ex} = 320$  nm.



**Figure S24.** RTP emission spectra of BrHB-Gla (dry), BrHB-Gla (wet), and BrHB (dry) and in the same condition. phosphorescence mode: Excitation slit = 10 nm; Emission slit = 10 nm. excitation voltage: 800 V. Excitation wavelength: 320 nm.

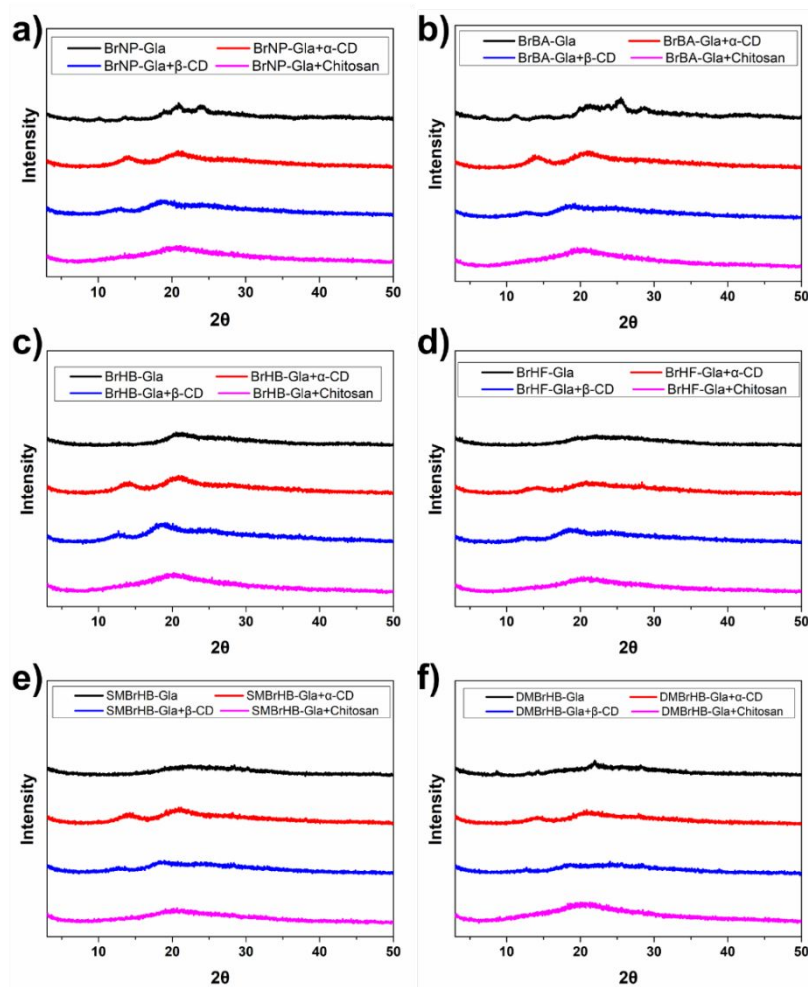


**Figure S25.** RTP emission spectrum and PL decay curves of a) BrNP- $\beta$ -CD,  $\lambda_{\text{ex}}$ =285nm,  $\lambda_{\text{em}}$ = 512 nm; b) BrHB- $\beta$ -CD,  $\lambda_{\text{ex}}$ = 300 nm,  $\lambda_{\text{em}}$ = 500 nm in amorphous solid state. Reproduced with permission from reference 45. Copyright 2018 American Chemical Society.

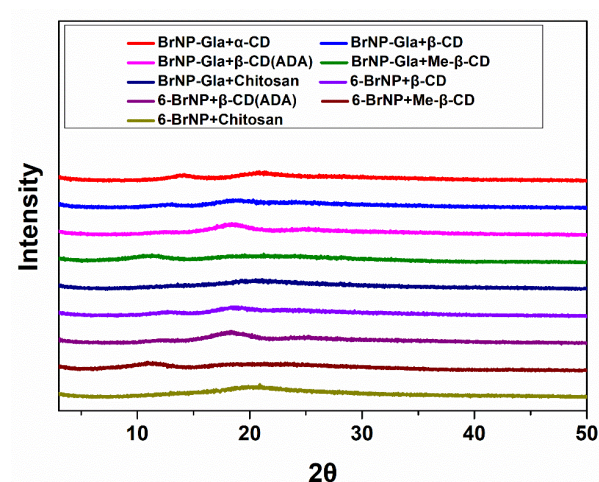
**Table S1.** Photophysical properties of BrNP- $\beta$ -CD, BrHB- $\beta$ -CD, BrNP-Gla, BrHB-Gla.

Phosphors	$\lambda_{\text{ex}}$ (nm)	$\lambda_{\text{em}}$ (nm)	$\tau_p$ (ms)	$\Phi_p$ (%)	$K_r$ (s <sup>-1</sup> )	$K_{\text{nr}}$ (s <sup>-1</sup> )
BrNP- $\beta$ -CD	285	512, 537	1.85	5.9	31.89	508.65
BrHB- $\beta$ -CD	300	500	0.96	2.8	29.17	1012.5
BrNP-Gla	337	605(roughly)	0.04	< 0.3	< 75	> 2.49×10 <sup>4</sup>
BrHB-Gla	320	540	0.14	0.8	57.14	7085.7

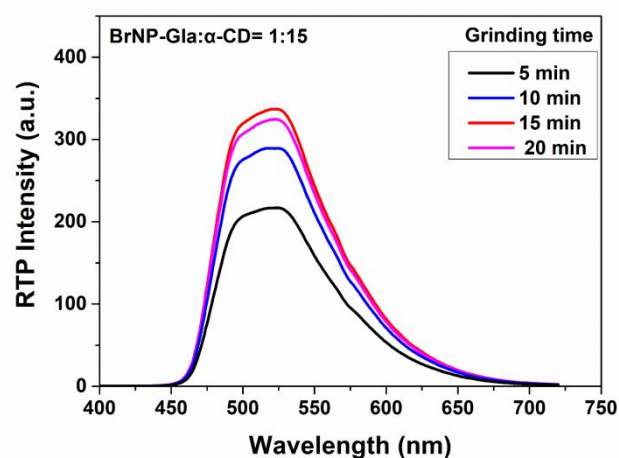
$K_r = \Phi_p / (\Phi_{\text{isc}} \tau_p)$ ;  $K_{\text{nr}} = (1 - \Phi_p / \Phi_{\text{isc}}) / \tau_p$ , due to the heavy atom effect,  $\Phi_{\text{isc}} \approx 1$ .



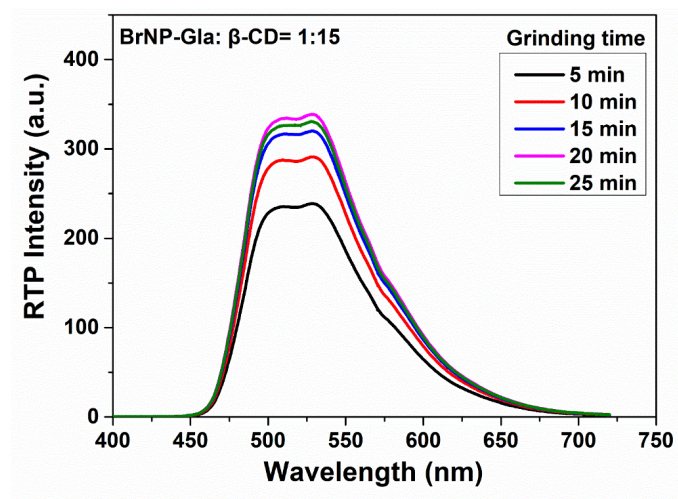
**Figure S26.** Powder X-ray diffraction (PXRD) patterns of a) BrNP-Gla, BrNP-Gla+ $\alpha$ -CD, BrNP-Gla+ $\beta$ -CD, and BrNP-Gla+Chitosan; b) BrBA-Gla, BrBA-Gla+ $\alpha$ -CD, BrBA-Gla+ $\beta$ -CD, and BrBA-Gla+Chitosan; c) BrHB-Gla, BrHB-Gla+ $\alpha$ -CD, BrHB-Gla+ $\beta$ -CD, BrHB-Gla+Chitosan; d) BrHF-Gla, BrHF-Gla+ $\alpha$ -CD, BrHF-Gla+ $\beta$ -CD, BrHF-Gla+Chitosan; e) SMBrHB-Gla, SMBrHB-Gla+ $\alpha$ -CD, SMBrHB-Gla+ $\beta$ -CD, SMBrHB-Gla+Chitosan; f) DMBRHB-Gla, DMBRHB-Gla+ $\alpha$ -CD, DMBRHB-Gla+ $\beta$ -CD, DMBRHB-Gla+Chitosan.



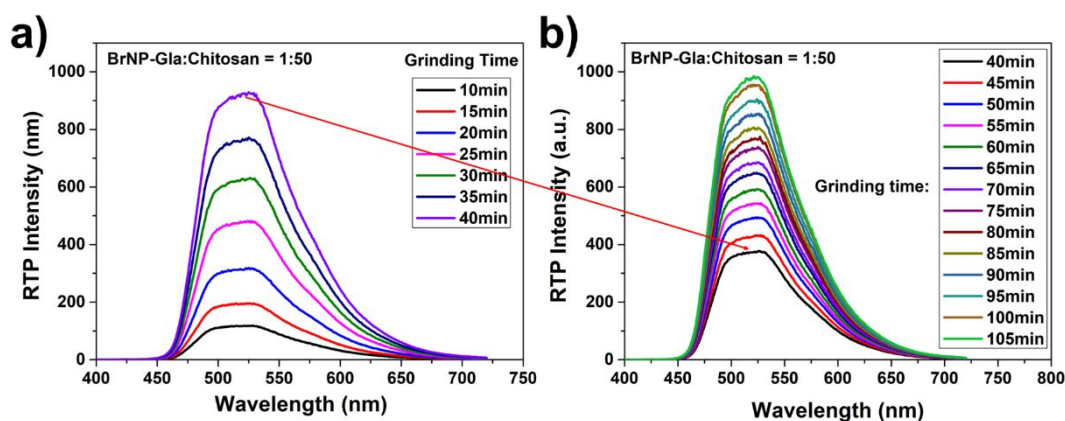
**Figure S27.** Powder X-ray diffraction (PXRD) patterns of BrNP-Gla+ $\alpha$ -CD, BrNP-Gla+ $\beta$ -CD, BrNP-Gla+ $\beta$ -CD(ADA), BrNP-Gla+Me- $\beta$ -CD, BrNP-Gla+Chitosan, 6-BrNP+ $\beta$ -CD, 6-BrNP+ $\beta$ -CD(ADA), 6-BrNP+Me- $\beta$ -CD, 6-BrNP+Chitosan.



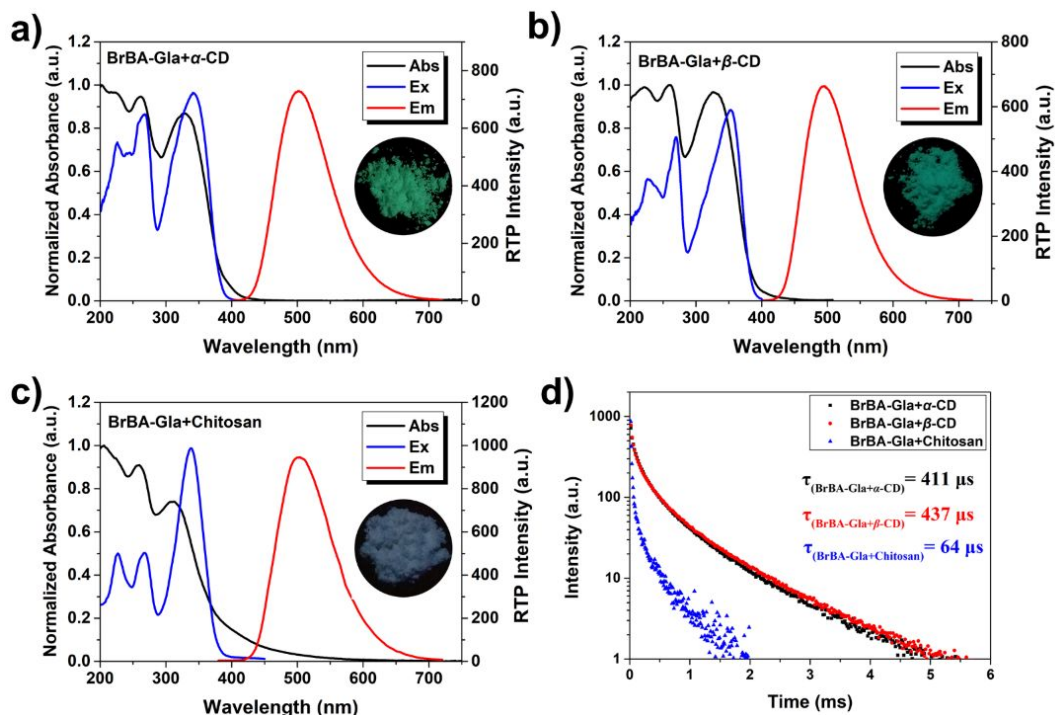
**Figure S28.** RTP emission spectrum of the mixture of BrNP-Gla and  $\alpha$ -CD (BrNP-Gla:  $\alpha$ -CD= 1: 15, mass ratio) for different grinding time. (phosphorescence mode; excitation slim = 10 nm; emission slim = 10 nm; excitation wavelength:  $\lambda_{\text{ex}}$ = 270 nm, excitation voltage: 430 V)



**Figure S29.** RTP emission spectrum of the mixture of BrNP-Gla and  $\beta$ -CD (BrNP-Gla:  $\beta$ -CD= 1: 15, mass ratio) for different grinding time. (phosphorescence mode; excitation slim = 10 nm; emission slim = 10 nm; excitation wavelength:  $\lambda_{\text{ex}}$ = 270 nm, excitation voltage: 450 V)

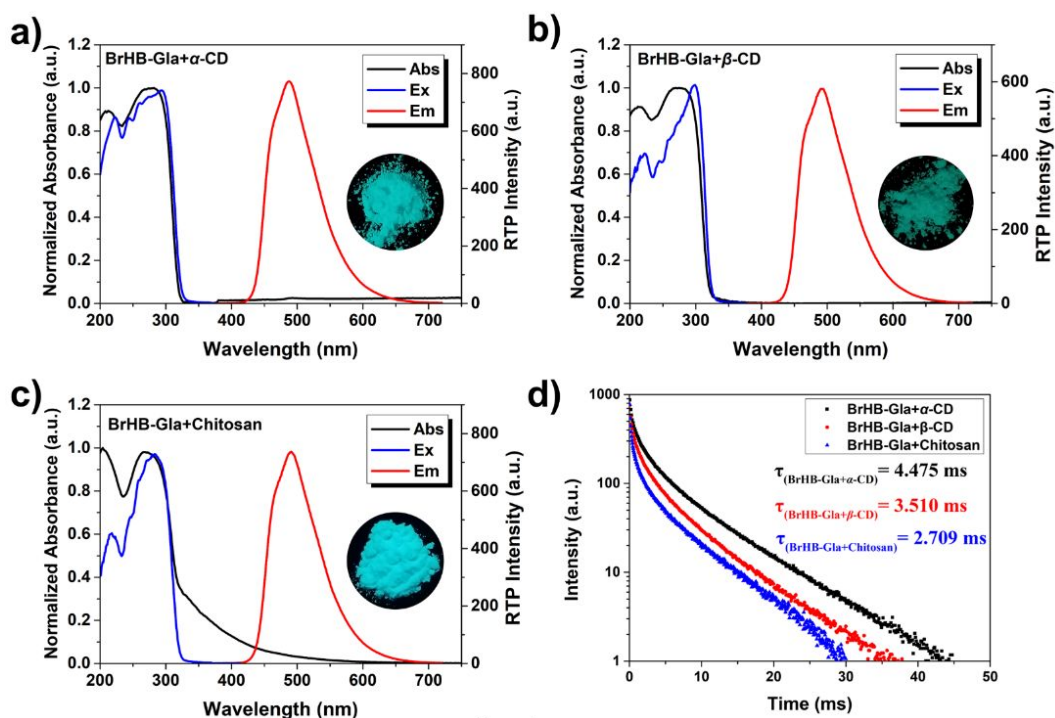


**Figure S30.** RTP emission spectrum of the mixture of BrNP-Gla and chitosan (BrNP-Gla: chitosan= 1: 50, mass ratio) for different grinding time. a) first 40 minutes; b) 40-105 minutes (phosphorescence mode; excitation slim = 10 nm; emission slim = 10 nm; excitation wavelength:  $\lambda_{\text{ex}}$ = 270 nm, excitation voltage: (a) 550 V (b) 500 V).



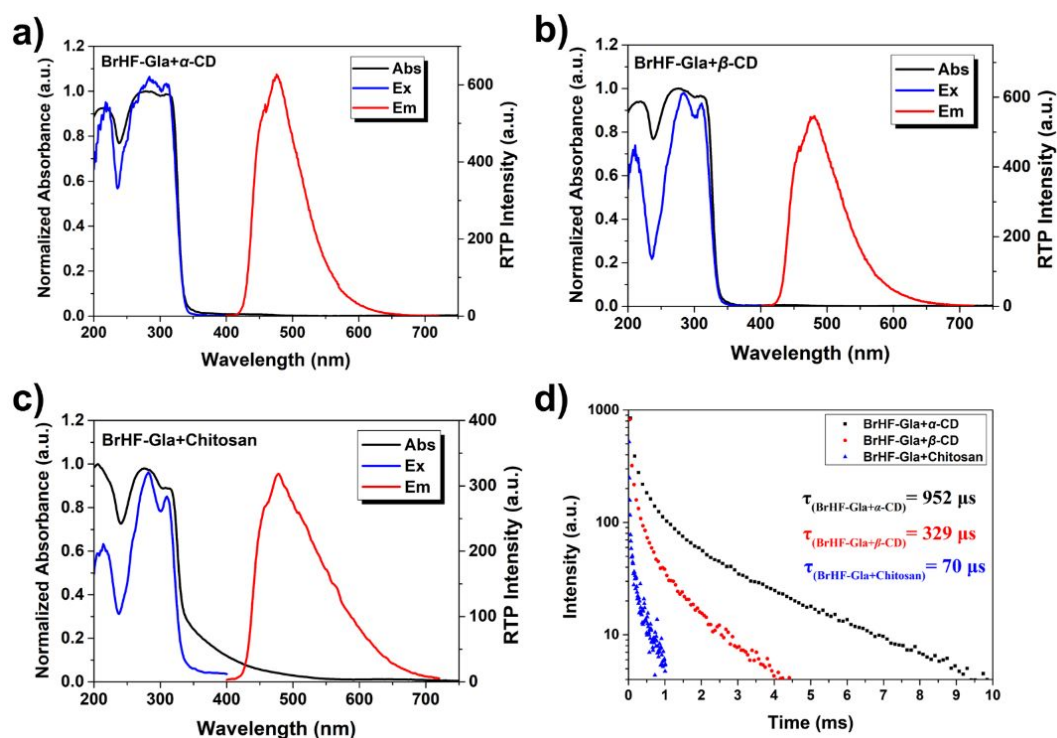
**Figure S31.** UV/Vis absorption (black), RTP emission (red) and excitation (blue) spectra of a) BrBA-Gla+ $\alpha$ -CD, b) BrBA-Gla+ $\beta$ -CD, and c) BrBA-Gla+Chitosan. (Phosphorescence mode; excitation wavelength of emission spectra: a) 341 nm, b) 353 nm, and c) 339 nm; emission wavelength of excitation spectra: a) 501 nm, b) 495 nm, and c) 503 nm; Inset: photographs of the samples under 254 nm light). d) PL decay time of BrBA-Gla+ $\alpha$ -CD at 501 nm, BrBA-Gla+ $\beta$ -CD at 495 nm, BrBA-Gla+Chitosan at 503 nm.



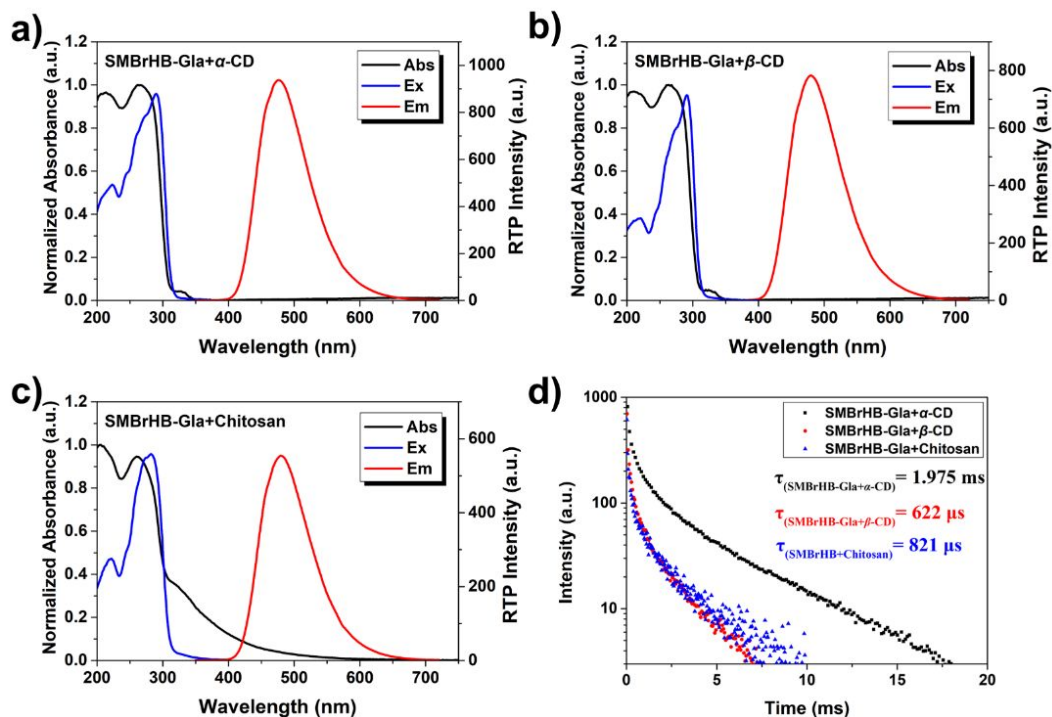


**Figure S32.** UV/Vis absorption (black), RTP emission (red) and excitation (blue) spectra of a) BrHB-Gla+ $\alpha$ -CD, b) BrHB-Gla+ $\beta$ -CD, and c) BrHB-Gla+Chitosan. (Phosphorescence mode; excitation wavelength of emission spectra: a) 294 nm, b) 294 nm, and c) 282 nm; emission wavelength of excitation spectra: a) 488 nm, b) 491 nm, and c) 491 nm; Inset: photographs of the samples under 254 nm light). d) PL decay time of BrHB-Gla+ $\alpha$ -CD at 488 nm, BrHB-Gla+ $\beta$ -CD at 491 nm, BrHB-Gla+Chitosan at 491 nm.

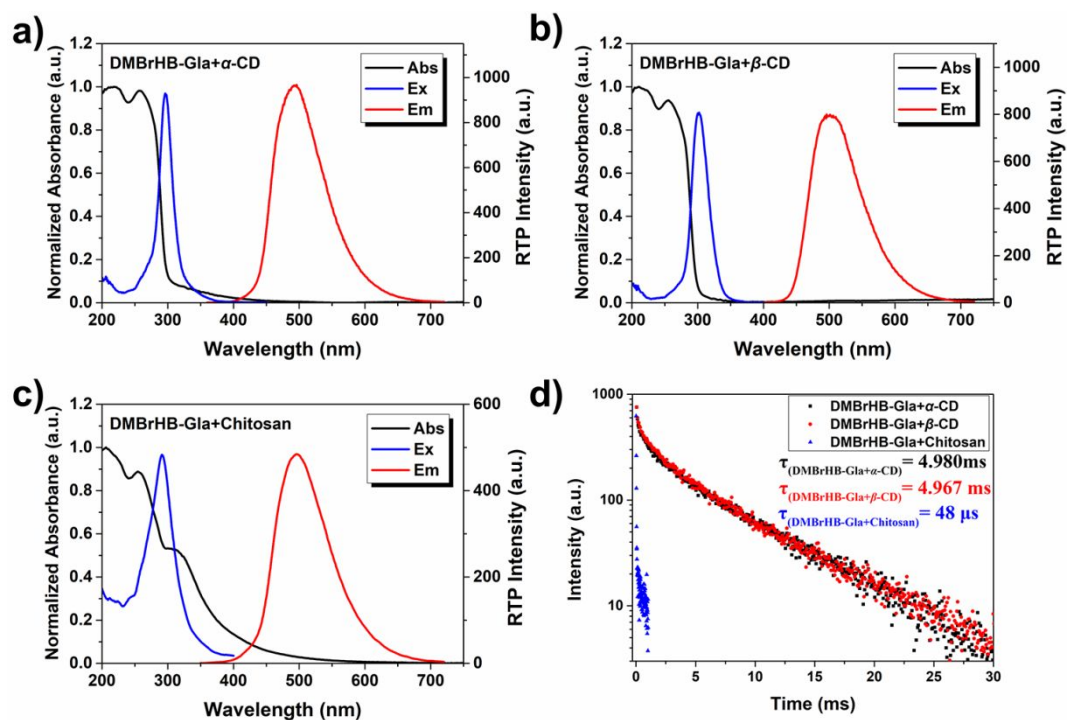




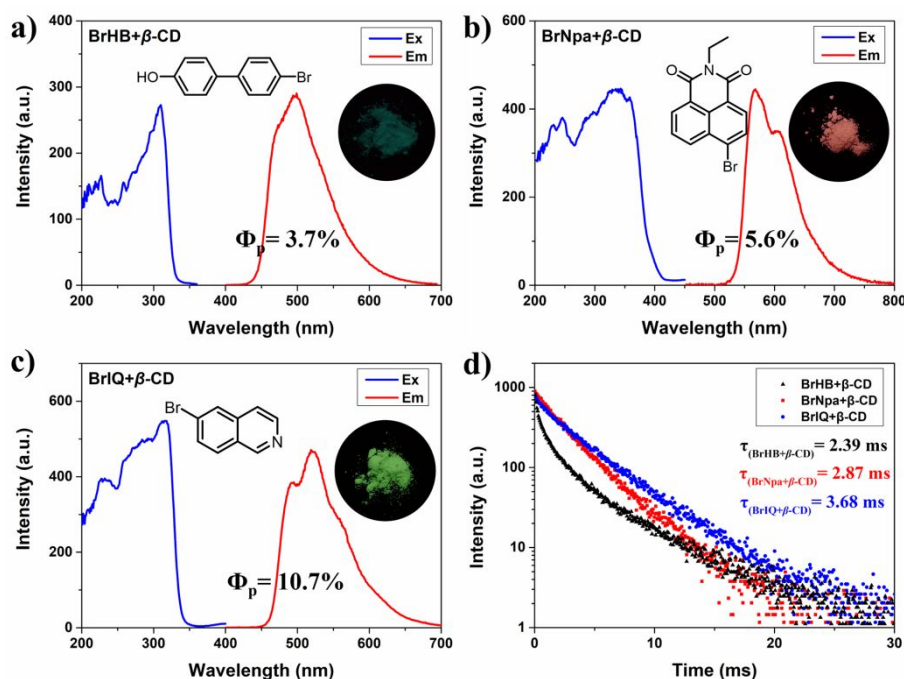
**Figure S33.** UV/Vis absorption (black), RTP emission (red) and excitation (blue) spectra of a) BrHF-Gla+ $\alpha$ -CD, b) BrHF-Gla+ $\beta$ -CD, and c) BrHF-Gla+Chitosan. (Phosphorescence mode; excitation wavelength of emission spectra: a) 284 nm, b) 285 nm, and c) 284 nm; emission wavelength of excitation spectra: a) 476 nm, b) 480 nm, and c) 478 nm). d) PL decay time of BrHF-Gla+ $\alpha$ -CD at 476 nm, BrHF-Gla+ $\beta$ -CD at 480 nm, BrHF-Gla+Chitosan at 478 nm.



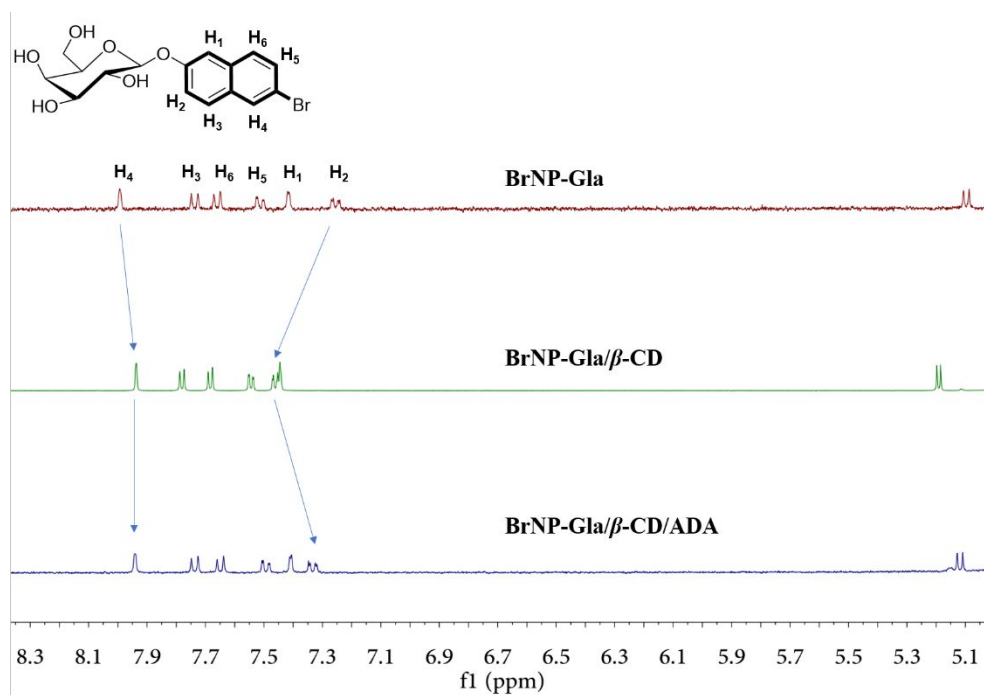
**Figure S34.** UV/Vis absorption (black), RTP emission (red) and excitation (blue) spectra of a) SMBrHB-Gla+ $\alpha$ -CD, b) SMBrHB-Gla+ $\beta$ -CD, and c) SMBrHB-Gla+Chitosan. (Phosphorescence mode; excitation wavelength of emission spectra: a) 291 nm, b) 291 nm, and c) 284 nm; emission wavelength of excitation spectra: 480 nm. d) PL decay time of SMBrHB-Gla+ $\alpha$ -CD, SMBrHB-Gla+ $\beta$ -CD, SMBrHB-Gla+Chitosan at 480 nm.



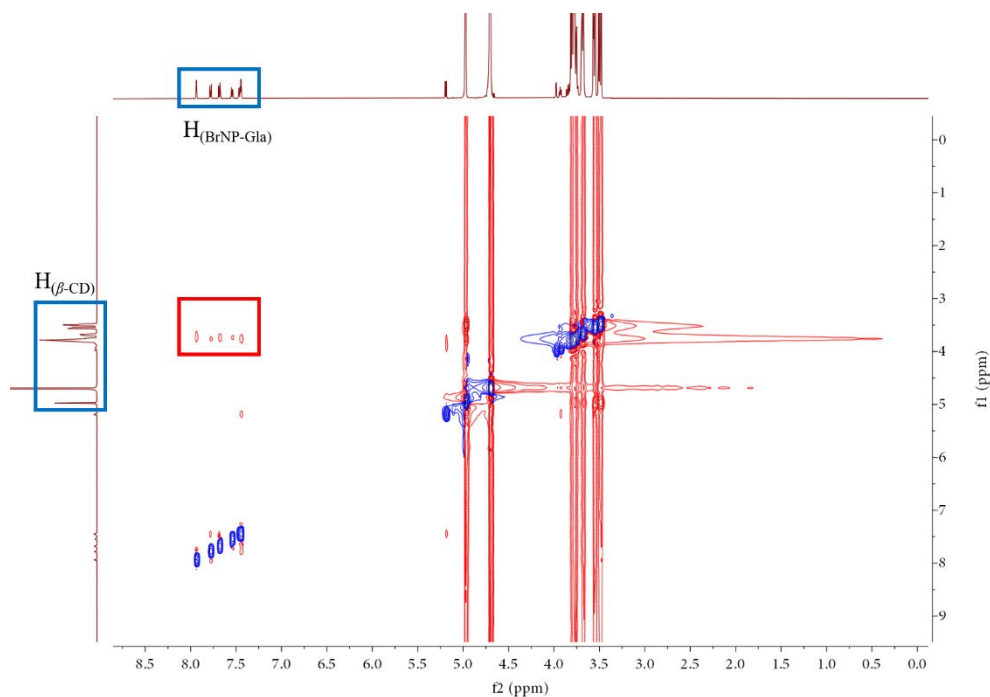
**Figure S35.** UV/Vis absorption (black), RTP emission (red) and excitation (blue) spectra of a) DMBrHB-Gla+ $\alpha$ -CD, b) DMBrHB-Gla+ $\beta$ -CD, and c) DMBrHB-Gla+Chitosan. (Phosphorescence mode; excitation wavelength of emission spectra: a) 296 nm, b) 300 nm, and c) 292 nm; emission wavelength of excitation spectra: a) 496 nm, b) 500 nm, and c) 496 nm). d) PL decay time of DMBrHB-Gla+ $\alpha$ -CD at 496 nm, DMBrHB-Gla+ $\beta$ -CD at 500 nm, DMBrHB-Gla+Chitosan at 496 nm.



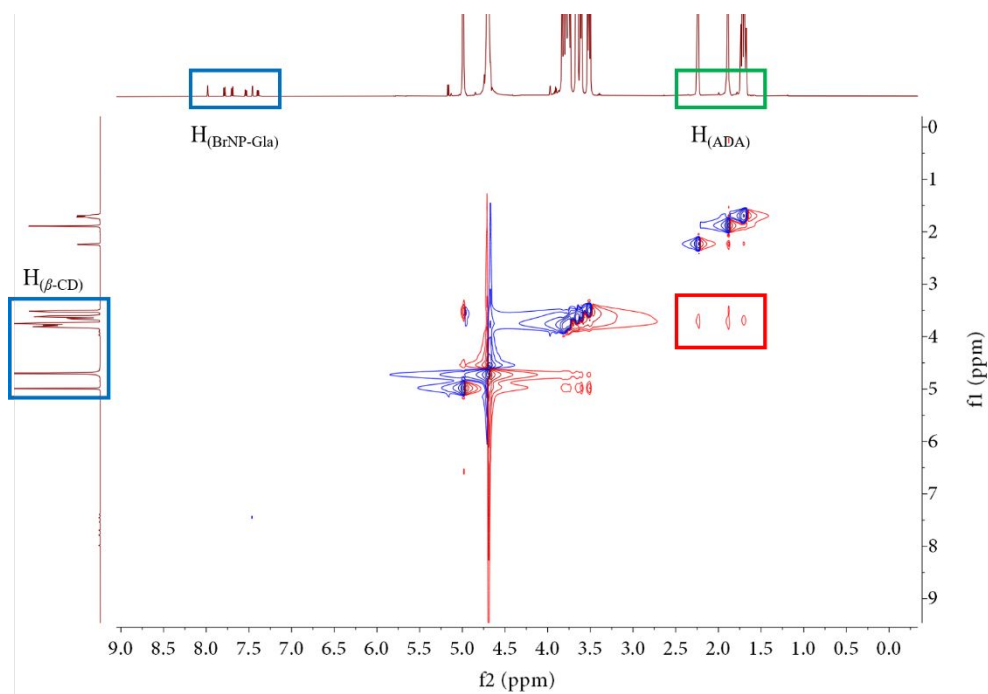
**Figure S36.** RTP emission (red) and excitation (blue) spectra of a) BrHB+β-CD, b) BrNpa+β-CD, and c) BrIQ+β-CD. (Phosphorescence mode; excitation wavelength of emission spectra: a) 294 nm, b) 340 nm, and c) 317 nm; emission wavelength of excitation spectra: a) 498 nm, b) 568 nm, and c) 519 nm; Inset: photographs of the samples under 254 nm (BrHB+β-CD, BrIQ+β-CD) and 365 nm (BrNpa+β-CD) light. d) PL decay time of BrHB+β-CD at 498 nm, BrNpa+β-CD at 568 nm, BrIQ+β-CD at 519 nm. This figure told the truth that such rigid matrices are effective to increase the RTP emission efficiency of usual phosphors by coassembling. Thereinto, the molar ratio between BrHB and β-CD was the same as BrHB-Gla+β-CD. The mass ratio of other assembling systems was 1:15.



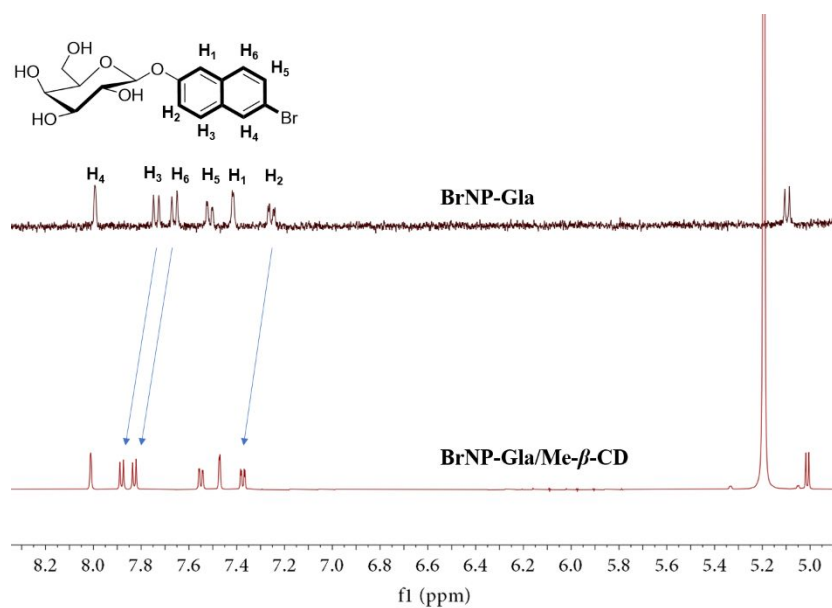
**Figure S37.** <sup>1</sup>H NMR spectrum of BrNP-Gla, saturated BrNP-Gla/β-CD (1/1 in molar ratio), and saturated solution of BrNP-Gla/β-CD/ADA (1/1/1 in molar ratio) in D<sub>2</sub>O.



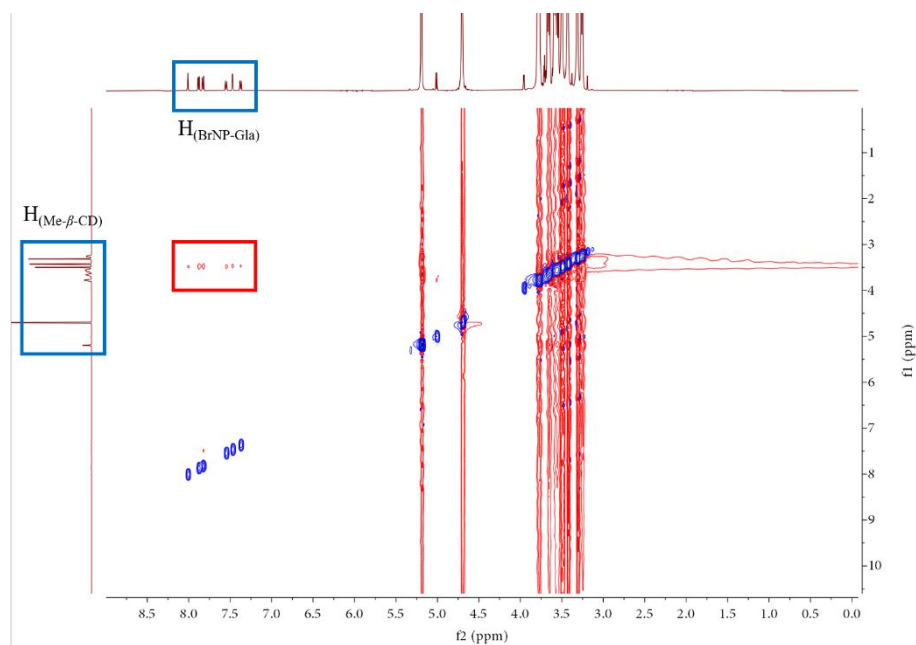
**Figure S38.** 2D ROESY spectrum of saturated BrNP-Gla/ $\beta$ -CD (1/1 in molar ratio) in D<sub>2</sub>O.



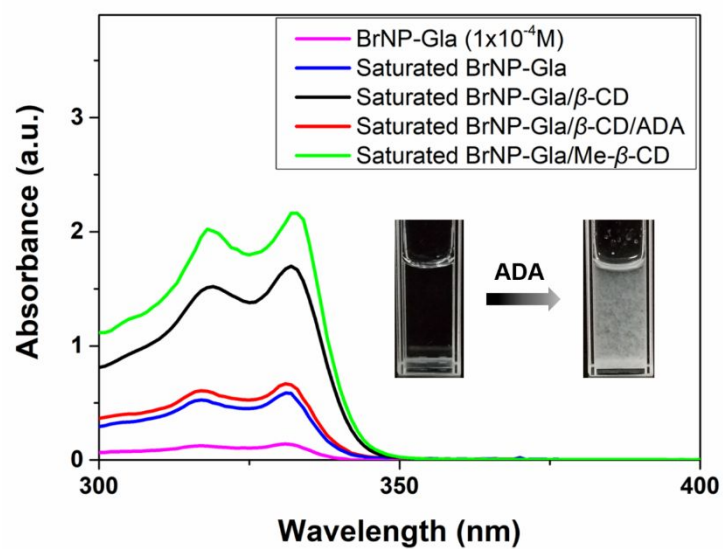
**Figure S39.** 2D ROESY spectrum of saturated BrNP-Gla/ $\beta$ -CD/ADA (1/1/1 in molar ratio) in D<sub>2</sub>O.



**Figure S40.**  $^1\text{H}$  NMR spectrum of BrNP-Gla, and saturated BrNP-Gla/Me- $\beta$ -CD (1/1 in molar ratio) in  $\text{D}_2\text{O}$ .

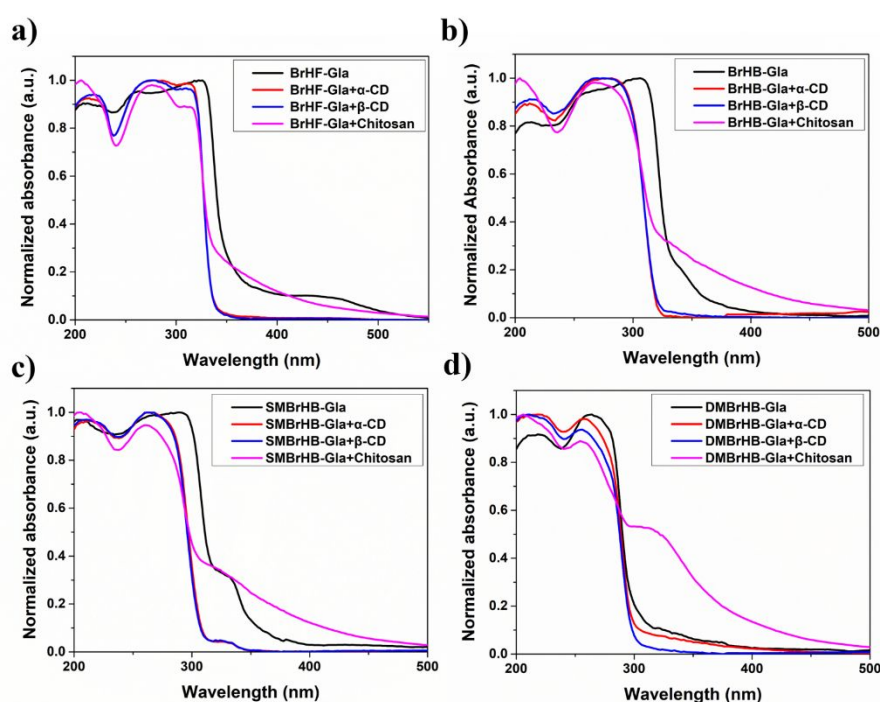


**Figure S41.** 2D ROESY spectrum of saturated BrNP-Gla/Me- $\beta$ -CD (1/1 in molar ratio) in  $\text{D}_2\text{O}$ .



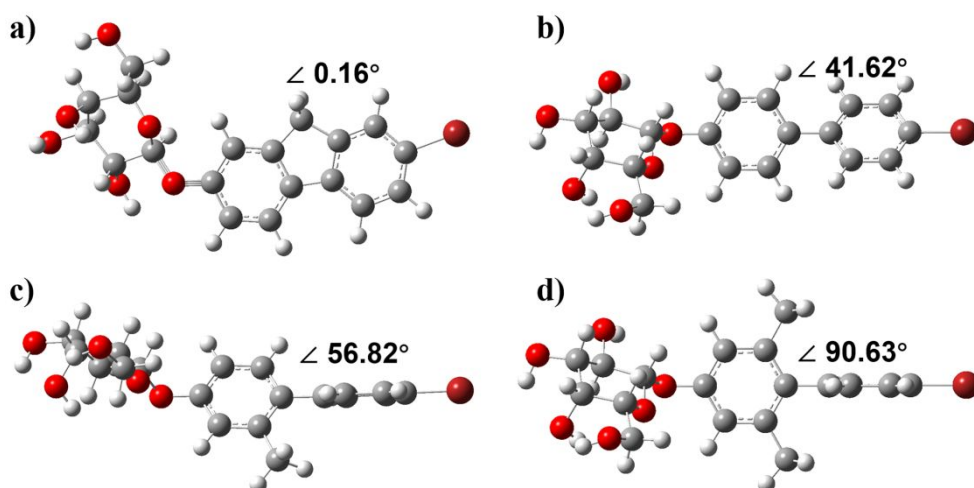


**Figure S42.** The absorption spectrum of aqueous BrNP-Gla solution ( $1 \times 10^{-4} \text{M}$ ), saturated BrNP-Gla solution, saturated solution of BrNP-Gla/ $\beta$ -CD (1/1 in molar ratio), saturated solution of BrNP-Gla/ $\beta$ -CD (1/1 in molar ratio) with ADA (1mg/mL), and saturated solution of BrNP-Gla/Me- $\beta$ -CD (1/1 in molar ratio). Inset: photographs of saturated solution of BrNP-Gla/ $\beta$ -CD before and after adding 1mg/mL ADA.



**Figure S43.** The absorption spectrum of a) BrHF-Gla, BrHF-Gla+ $\alpha$ -CD, BrHF-Gla+ $\beta$ -CD, BrHF-Gla+Chitosan; b) BrHB-Gla, BrHB-Gla+ $\alpha$ -CD, BrHB-Gla+ $\beta$ -CD, BrHB-Gla+Chitosan; c) SMBrHB-Gla, SMBrHB-Gla+ $\alpha$ -CD, SMBrHB-Gla+ $\beta$ -CD, SMBrHB-Gla+Chitosan; d) DMBrHB-Gla, DMBrHB-Gla+ $\alpha$ -CD, DMBrHB-Gla+ $\beta$ -CD, DMBrHB-Gla+Chitosan.





**Figure S44.** Optimized BrHF-Gla, BrHB-Gla, SMBrHB-Gla, DMBrHB-Gla structure at ground state calculated by B3LYP/6-311G\*, and the dihedral angles of phenyls.

	BrNP-Gla	BrBA-Gla	BrHB-Gla	BrHF-Gla	SMBrHB-Gla	DMBrHB-Gla
LUMO						
HOMO						
LUMO	-1.76 eV	-2.60 eV	-1.49 eV	-1.44 eV	-1.29 eV	-1.01 eV
HOMO	-6.33 eV	-7.04 eV	-6.57 eV	-6.10 eV	-6.63 eV	-6.88 eV
HOMO-LOMO Gap	4.57 eV	4.45 eV	5.07 eV	4.66 eV	5.34 eV	5.87 eV
$S_1$	3.49 eV	3.13 eV	3.63 eV	3.71 eV	3.55 eV	3.81 eV
$T_1$	1.90 eV	2.17 eV	2.07 eV	2.20 eV	2.03 eV	2.39 eV
$\Delta E_{ST}$	1.59 eV	0.96 eV	1.56 eV	1.51 eV	1.52 eV	1.42 eV
$S_1^*$	4.04 eV	3.54 eV	4.66 eV	4.19 eV	4.80 eV	5.05 eV
$T_1^*$	2.74 eV	3.00 eV	3.24 eV	2.98 eV	3.42 eV	3.63 eV

**Figure S45.** Frontier orbitals of optimized BrNP-Gla, BrBA-Gla, BrHB-Gla, BrHF-Gla, SMBrHB-Gla, DMBrHB-Gla structure at ground state calculated by B3LYP/6-311G\*; Calculated energy for HOMO, LUMO, and energy gap from

HOMO to LUMO based on the optimized ground state structure; Calculated energy of first excited singlet state ( $S_1$ ), first excited triplet state ( $T_1$ ), and the energy gap between  $S_1$  and  $T_1$  ( $\Delta E_{ST}$ ) based on the optimized  $T_1$  state structure; Calculated energy of first excited singlet state ( $S_1^*$ ) and first excited triplet state ( $T_1^*$ ) based on the optimized ground state structure.