

## Electronic Supplementary Information

### Separation of Lead-212 from Natural Thorium Solution Utilizing Novel Sulfonamide Dibenzo-18-crown-6†

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#### 1. SYNTHESIS SECTION

##### 1.1. Synthesis of 2,13-disulfo(di-tetramethylammonium) dibenzo-18crown-6 (DSDB18C6)

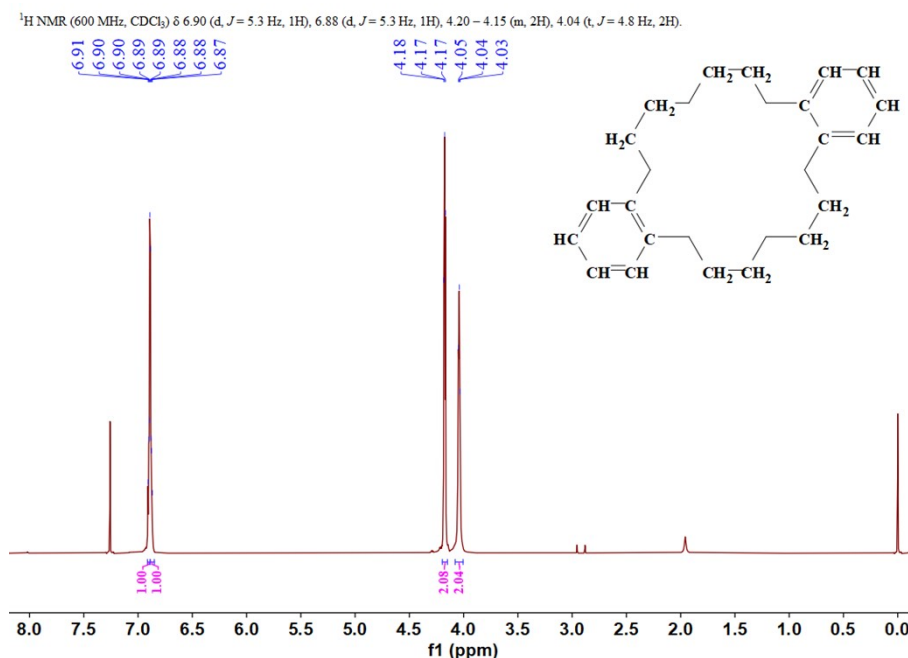
DSDB18C6 was synthesized by an improved version of the method reported by Sasaki<sup>1</sup>. When 3.6 g of dibenzo 18 crown 6 (10 mmol) and 50 mL of acetonitrile were magnetically stirred in a round-bottom flask, a part of the material remained undissolved. Subsequently, 2.0 g of sulfuric acid (98%, 20 mmol) was slowly added from a dropping funnel at room temperature. The mixture was then refluxed and stirred for 24 hours at 82 °C. As the white precipitate completely dissolved, a substantial amount of bright yellow oil gradually formed in the flask. The excess solvent was evaporated under vacuum, and the crude product was precipitated by adding a 7.4 mL methanol solution of tetramethylammonium hydroxide (25%, 20 mmol). DSDB18C6 was subjected to two rounds of crystallization in a mixture of methanol and ethyl acetate (v/v = 3/7), followed by vacuum drying, yielding 81%. <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O) δ 7.36 (d, *J* = 10.4 Hz, 2H), 7.30 (s, 2H), 7.00 (d, *J* = 8.5 Hz,

2H), 4.18 – 4.10 (m, 8H), 3.88 (t,  $J = 5.2$  Hz, 8H), 3.10 (s, 32H). FT-IR (KBr): 1325 and 1150  $\text{cm}^{-1}$  ( $-\text{SO}_3^-$ ).

## 1.2. Synthesis of 2,13-disulfonyl chloride dibenzo-18crown-6 (DSCIDB18C6)<sup>2</sup>

Firstly, 2.0 g of DSDB18C6 (3 mmol) was dissolved in 30 mL of boiling DMF with magnetic stirring and then cooled to room temperature. 1.0 g of sulfoxide dichloride (8.2 mmol) was added dropwise while maintaining an ice-water bath, and the resulting mixture was stirred at room temperature for 12 hours. The milky mixture was gently poured into 100 mL of ice water, leading to the formation of a white precipitate. Thoroughly the precipitate was rinsed with deionized water, followed by vacuum drying under a temperature of 40 °C, resulting in the formation of DSCIDB18C6 with a yield of 92%. FT-IR (KBr) 1370 and 1175  $\text{cm}^{-1}$  (S=O), 550  $\text{cm}^{-1}$  (S-Cl).

## 2. CHARACTERIZATION SECTION



**Figure S1** <sup>1</sup>H NMR spectrum of DB18C6.

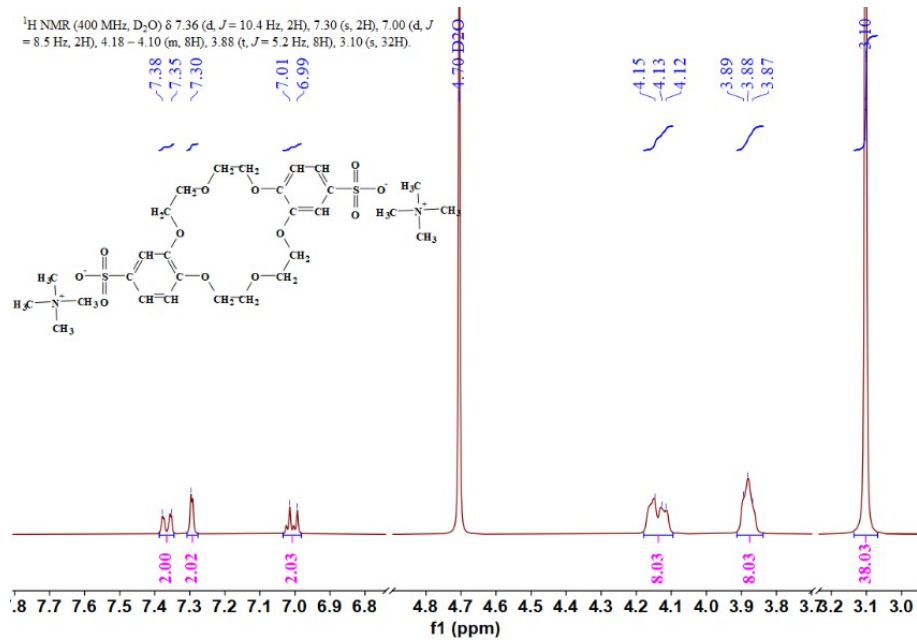


Figure S2 <sup>1</sup>H NMR spectrum of DSDB18C6.

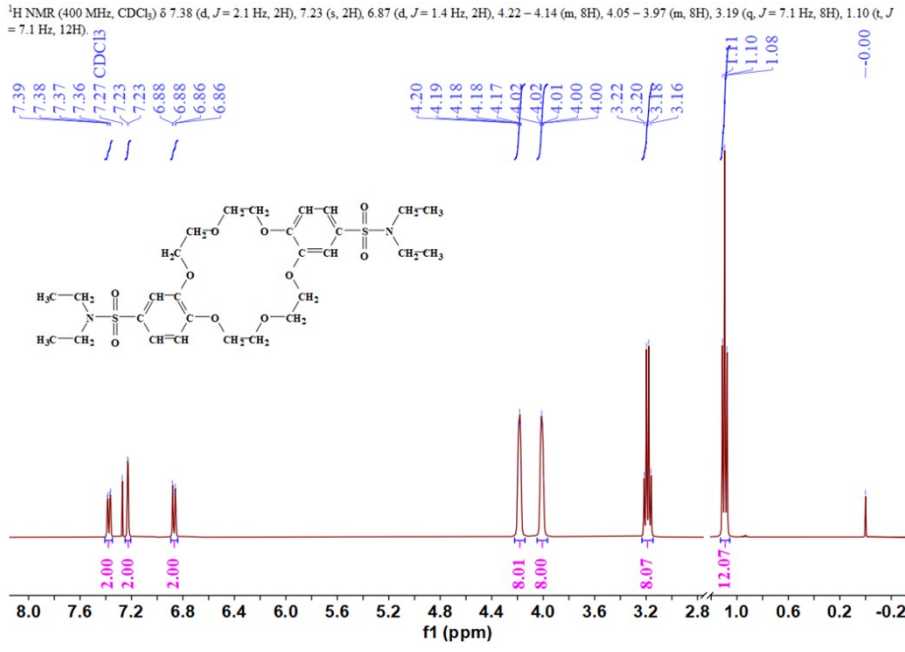


Figure S3 <sup>1</sup>H NMR spectrum of DSADB18C6.

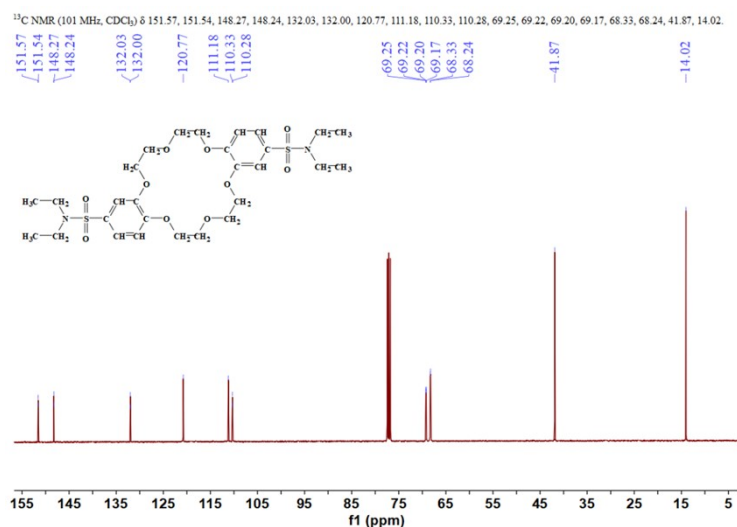


Figure S4 <sup>13</sup>C NMR spectrum of DSADB18C6.

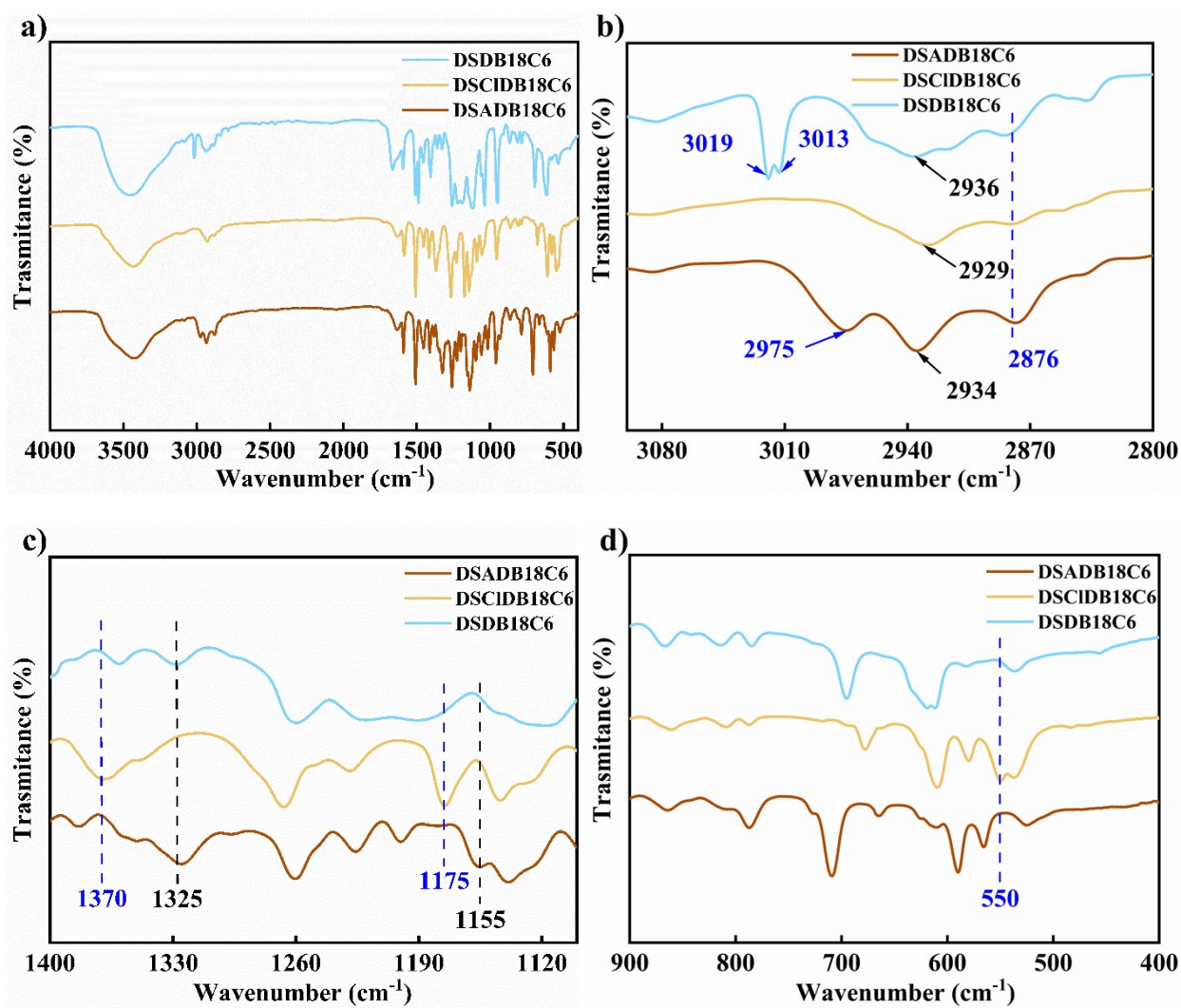
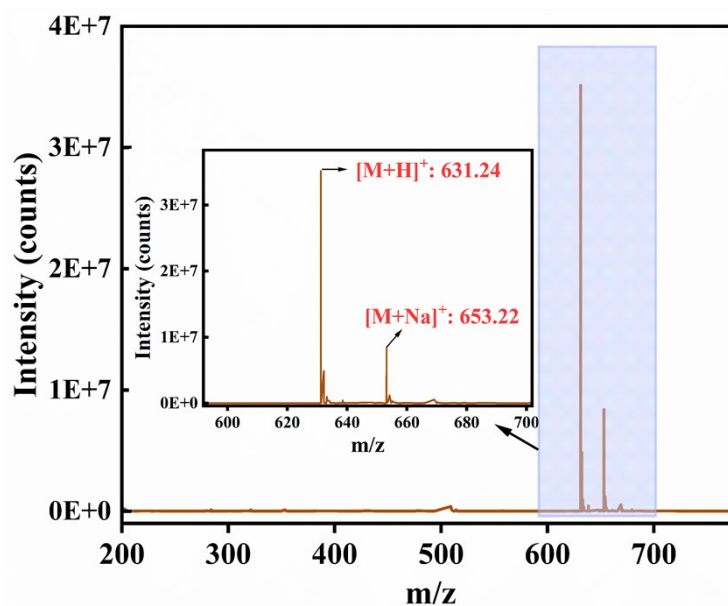


Figure S5 FT-IR spectra of DSDB18C6, DSCIB18C6 and DSADB18C6.



**Figure S6** ESI-MS spectrum of DSADB18C6.

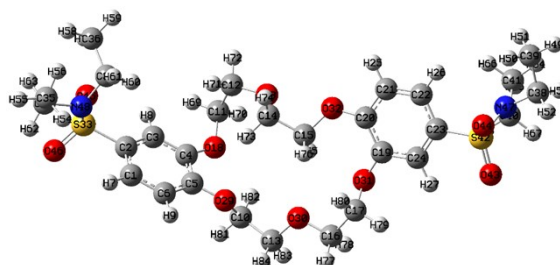
**Table S1** Characteristic FT-IR spectral data for DSDB18C6, DSCIDB18C6 and DSADB18C6 (corresponding to **Figure S5**).

Probable assignment	Wavenumber (cm <sup>-1</sup> )		
	DSDB18C6	DSCIDB18C6	DSADB18C6
$\nu_{as}$ C-H (-CH <sub>3</sub> )	3019, 3013	/	2975
$\nu_{as}$ C-H (Ar-H)	2936	2929	2934
$\nu_s$ C-H	2877	2876	2874
$\nu_{as}$ O=S-Cl	/	1370	/
$\nu_s$ O=S-Cl	/	1175	/
$\nu_{as}$ O=S-N	1325	/	1325
$\nu_s$ O=S-N	/	/	1155
$\nu$ S-Cl	/	550	/

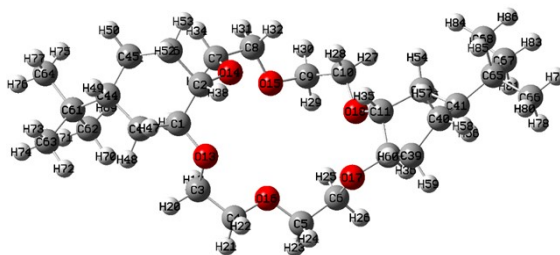
**Table S2** m/z peak positions and probable molecular formulae (corresponding to **Figure S6**).

System	m/z peak	Probable molecular formula
Chloroform	631.24	DSADB18C6+H <sup>+</sup>
	653.22	DSADB18C6+Na <sup>+</sup>

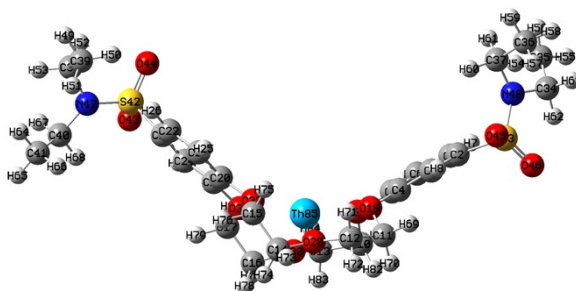
## 2. CALCULATION SECTION



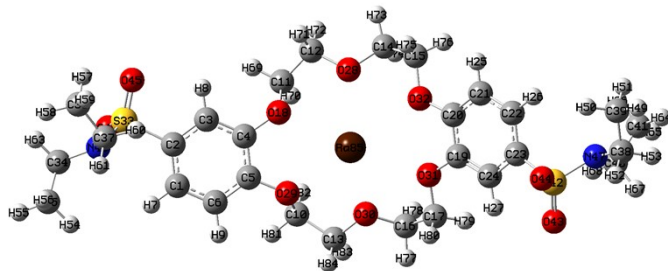
**Figure S7** Optimized geometries of studied DSADB18C6 central view at DFT level of theory.



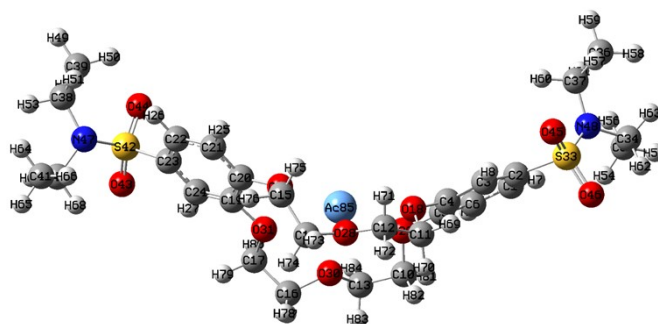
**Figure S8** Optimized geometries of studied DtBuDC18C6 central view at DFT level of theory.



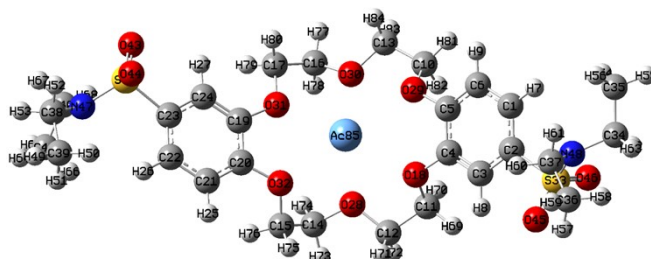
**Figure S9** Optimized geometries of studied DSADB18C6-Th lateral view at DFT level of theory.



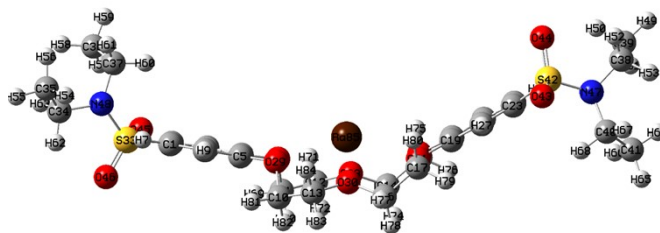
**Figure S10** Optimized geometries of studied DSADB18C6-Th central view at DFT level of theory.



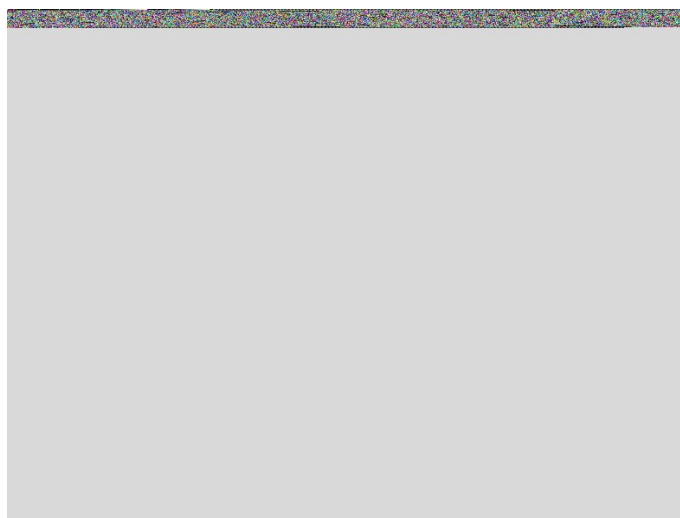
**Figure S11** Optimized geometries of studied DSADB18C6-Ac lateral view at DFT level of theory.



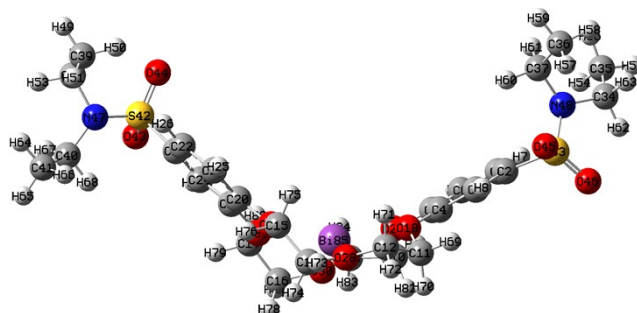
**Figure S12** Optimized geometries of studied DSADB18C6-Ac central view at DFT level of theory.



**Figure S13** Optimized geometries of studied DSADB18C6-Ra lateral view at DFT level of theory.

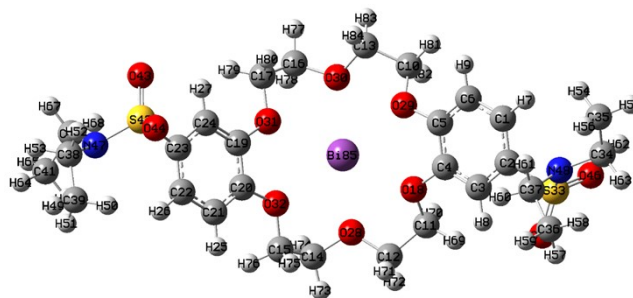


**Figure S14** Optimized geometries of studied DSADB18C6-Ra central view at DFT level of theory.



**Figure S15** Optimized geometries of studied DSADB18C6-Bi lateral view at DFT level of theory.

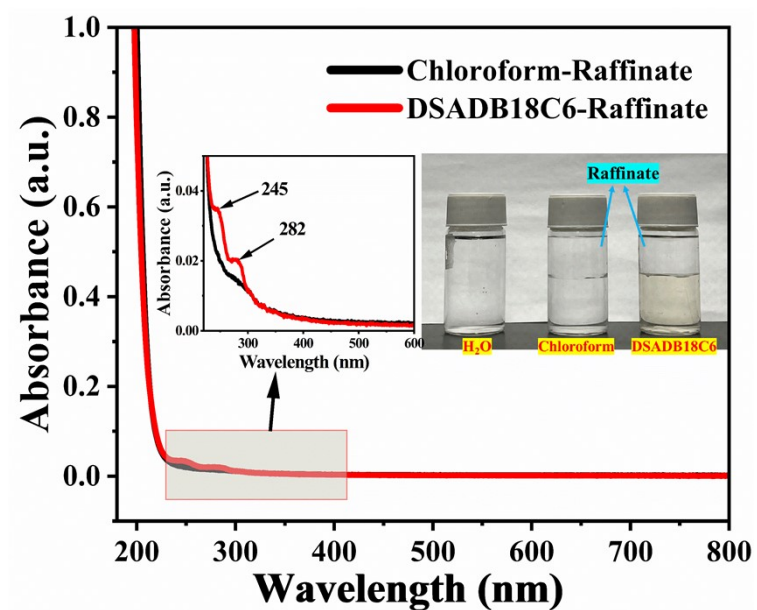




**Figure S16** Optimized geometries of studied DSADB18C6-Bi central view at DFT level of theory.

#### 4. LEACHING OF THE EXTRACTANT

A 10 mL sample of DSADB18C6 chloroform solution with a concentration of 20 mmol/L was mixed with an equal volume of ultrapure H<sub>2</sub>O and shaken to mix thoroughly. The mixture was allowed to naturally separate under gravity, and the upper raffinate was extracted for UV spectroscopy testing. Concurrently, control samples were prepared by extracting the aqueous phase using pure chloroform solvent, while blank samples were created using deionized water. The UV spectroscopy results obtained are depicted in Figure S15. The small window provides a clear view of the upper aqueous phase appearing colorless and transparent, while the chloroform phase containing DSADB18C6 exhibits a pale-yellow color. This signifies the absence of any visible leakage of the extraction agent into the aqueous phase. The UV spectrum indicates a slight absorption peak at 245nm and 282 nm in the red line, attributed to the characteristic absorption of DSADB18C6. However, the peak is not particularly prominent, which indicates that the residual extract contains a very small amount of DSADB18C6. Therefore, it is unlikely to cause significant secondary pollution in the required separation and purification process.



**Figure S17** UV spectra of the raffinate. Organic phase: chloroform, chloroform solution for DSADB18C6; aqueous: H<sub>2</sub>O. [DSADB18C6] = 20 mmol/L,  $T = 298 \pm 1$  K,  $t = 30$  min.

## 5. REFERENCES

1. T. Sasaki, S. Umetani, M. Matsui, S. Tsurubou, T. Kimura and Z. Yoshida, *Bulletin of the Chemical Society of Japan*, 1998, **71**, 371-377.
2. S. Shinkai, T. Minami, Y. Araragi and O. Manabe, *Journal of the Chemical Society, Perkin Transactions 2*, 1985, **5**, 503-509.