Supporting Information

On the Study of Cucurbit[6]uril and 4-tert-Butylcalix[6]arene for Multifunctional Lubricant Additives

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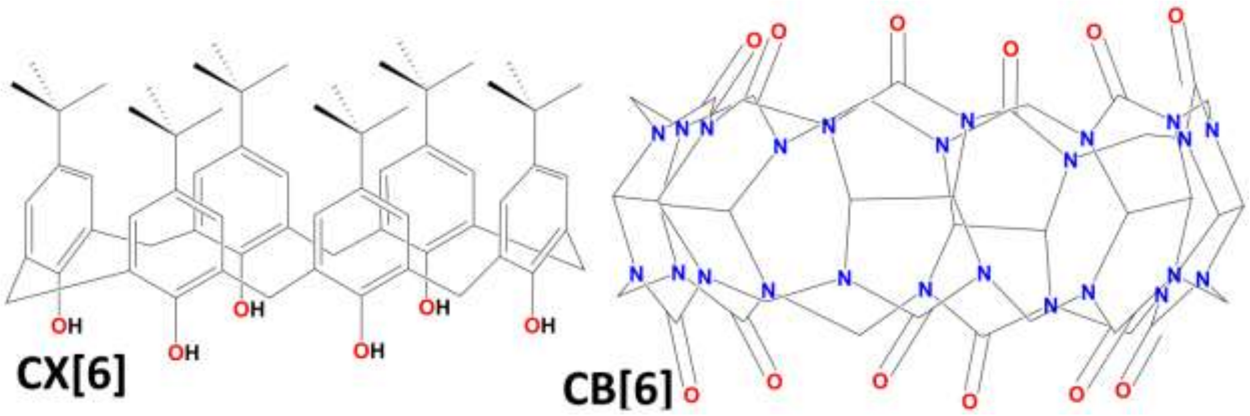


Figure S1. Showing structure of CX[6] &CB[6]

The molecular height of CB[6] is ~9.1 Å with diameter ~5.8 Å and inner ~3.9 Å. while CX[6] cavity diameter is 7.6 Å.

Synthesis of Glycoluril and CB[6]

Glycouril was synthesized according to the literature reported by Beherend and its coworkers some 75 years ago. Urea (46g) was taken in a 500 ml RB flask and 250 ml water was used to fully dissolve that 8-10 M conc. HCl was added with stirring about 30min, reaction temperature was maintained at 75^{O}C and then 10 ml glyoxal solution was added drop by drop. The reaction mixture was then kept at 75^{O}C for next 1-2 hrs, stirring until heavy white ppt. appears. After cooling, the resulting solution was filtered, washed successively with water 2-3 times and then water was removed by adding acetone 3-4 times. The obtained organic product then dried at 60^{O}C for 6 hrs vacuum. The small portion of obtained product was further treated with excess of formaldehyde but the product obtained was not showing satisfactory results. The filterate obtained can be used again for capturing all glyoxal left in the mixture by adding urea in excess, this may increase yield up to 80%. Inspite of ^{1}HNMR, satisfactory results were also obtained by getting melting point at 280^{O}C.

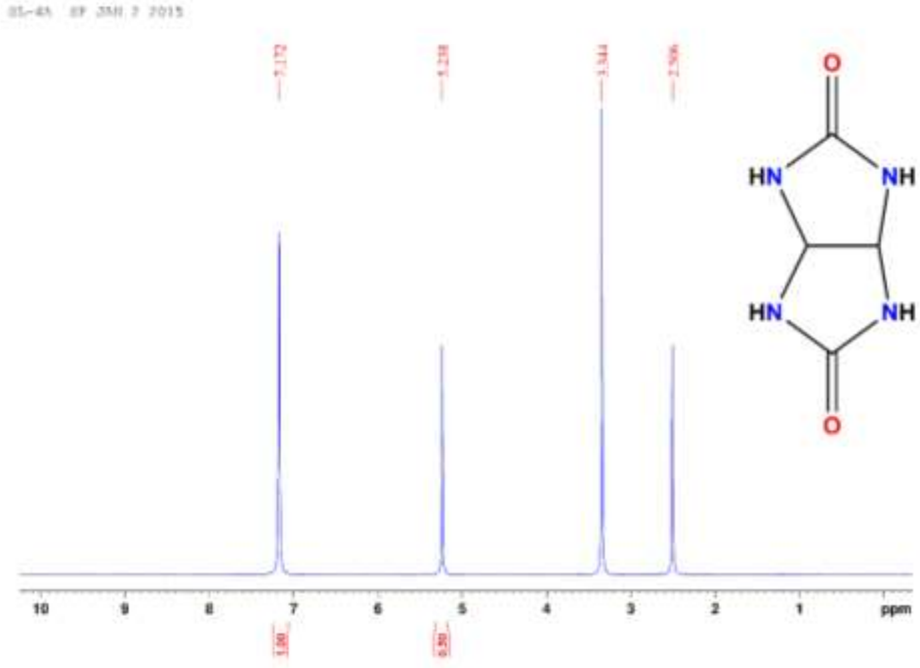


Figure S2. Showing ^{1}HNMR results of Glycoluril in DMSO-d_6 (2.506 δ), 5.238 δ (S, 2H), 7.172 (S,4H).

For the synthesis of CB[6] 7.1 g glycouril was added in a 500 ml two necked round bottom flask equipped with a thermometer, reflux condenser and 9M H_2SO_4 (50 ml) was added and then 15 ml 40% formaldehyde solution was added. There after reactor was heated to 100-105^{O}C for next 24 hrs with constant stirring and then for next 12 hrs at 110^{0}C. The reaction mixture was then cooled to room temperature and first precipitate was collected out, filterate further treated for fractional addition of acetone and water results in CB[6] precipitate formation which was collected and dried. At every step reaction result was purified by filtering off and washing with acetone.

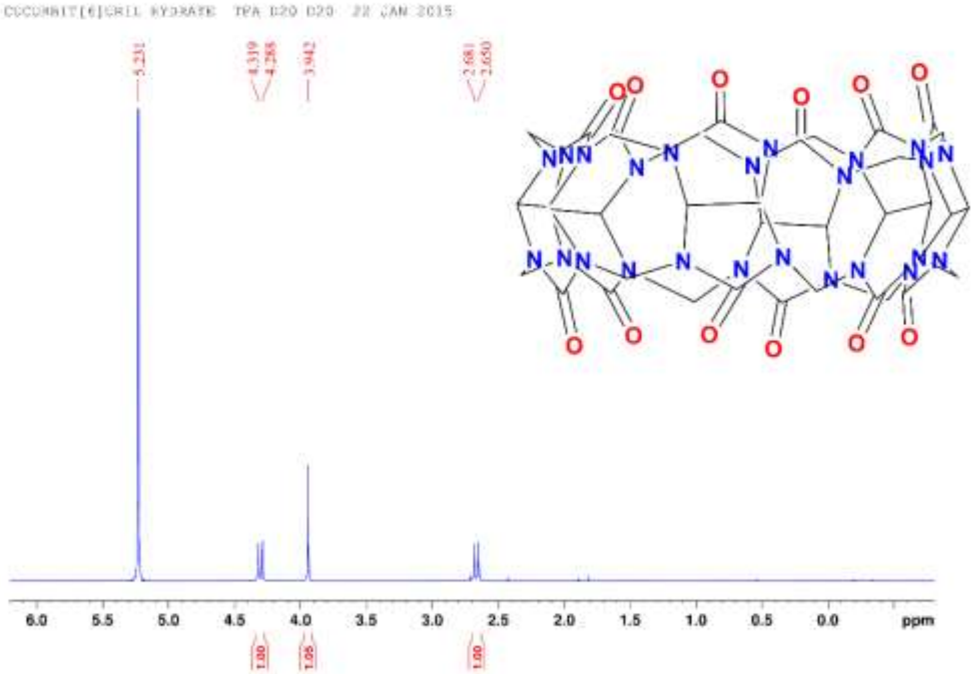


Figure S3. Showing CB[6] ^{1}HNMR (500 MHz, $D_2O/CF_3\text{-}CO_2D$ (1:1) : 4.47 δ (d, 12H, *J*= 15.5 Hz), 4.112 δ (s, 12H), 2.82 δ (d, 12H, *J* = 15.5 Hz). Locked in D_2O (5.1005 δ)

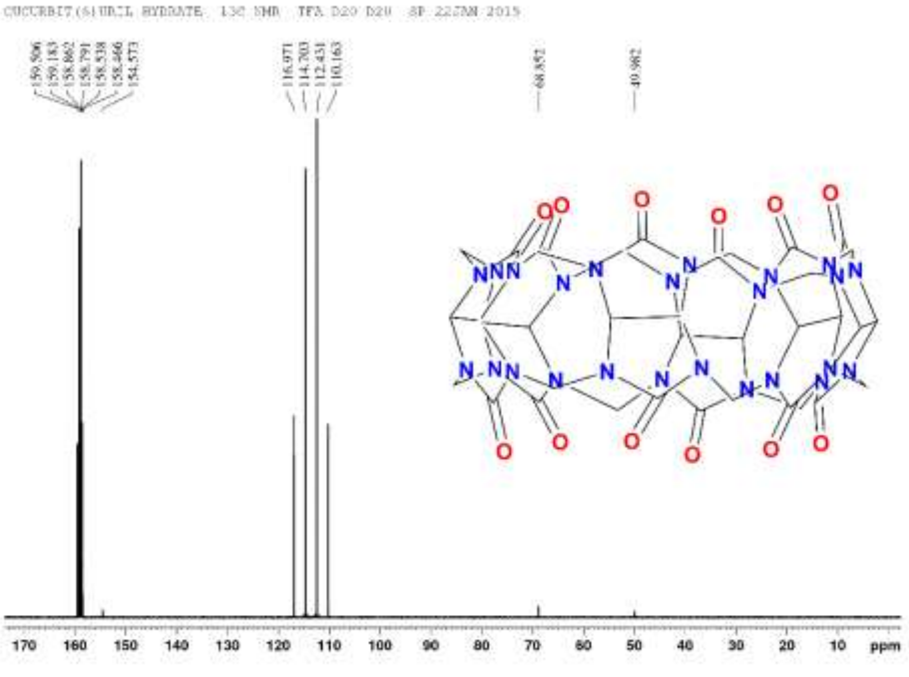
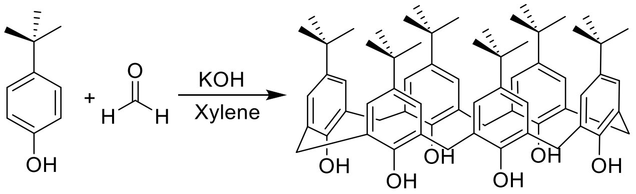


Figure S4. Showing CB[6] ^{13}CNMR (500 MHz, $D_2O/CF_3\text{-}CO_2D$ (1:1) : 154.57 δ (12C), 68.852 δ (12C), 49.982 δ (12C). Locked in D_2O.

Preparation of *t*-Butyl Calix[6] arene:



The Literature procedure was showing poor results as far as purity and yield, hence the procedure was optimized that is reproducible at various scales.

In a typical modified procedure, a mixture of 10 g (0.06mol) of p-tert-butylphenol, 13.5 mL of 37% formaldehyde solution and 1.5 gm of KOH (0.227mole) was stirred in 1 L, 3 necked, round-bottomed flask with a mechanical stirrer. Heat the mixture at 12 ^{0}C for two hours. Nitrogen is blown across the reaction mixture at a brisk rate during this period. During this period clear solution turn light yellow and finally changes to semisolid mass. (This step is most important step of this reaction. So, must perform carefully. Water should be removed completely. Presence of small amount of it could cause the formation of calix[8]arene, which is difficult to separate).Xylene (100mL) is now added to the flask to dissolve the semisolid mass and give a yellow solution that is brought quickly to reflux by increasing the temperature of the heating mantle. (Water should be removed quickly. In this step Dean stark trap should be used). After 30 minute precipitate begins to form and color of reaction mixture changes from yellow to orange. Reflux the mixture for 3 hours.The mixture is allowed to cool to room temperature. The mixture is filtered, and the precipitate is washed with xylene and dried on a Büchner funnel. The mixture is allowed to cool and filtered. 5gm of white powder is obtained. M.P = 372°C.The purity of the product can be qualitatively checked with TLC using a petroleum ether /methylene chloride mixture (60 : 40) as eluent. The $R_f$of the cyclic hexamer is ca. 0.65. Yield = 9.0gm (84.1%). Melting Point -380-381ºC.^{1}H NMR ($CDCl_3$)δ: 1.25 (s, 54 H), 3.90 (s, 12 H), 7.14 (s, 12 H), 10.53 (s, 6 H).

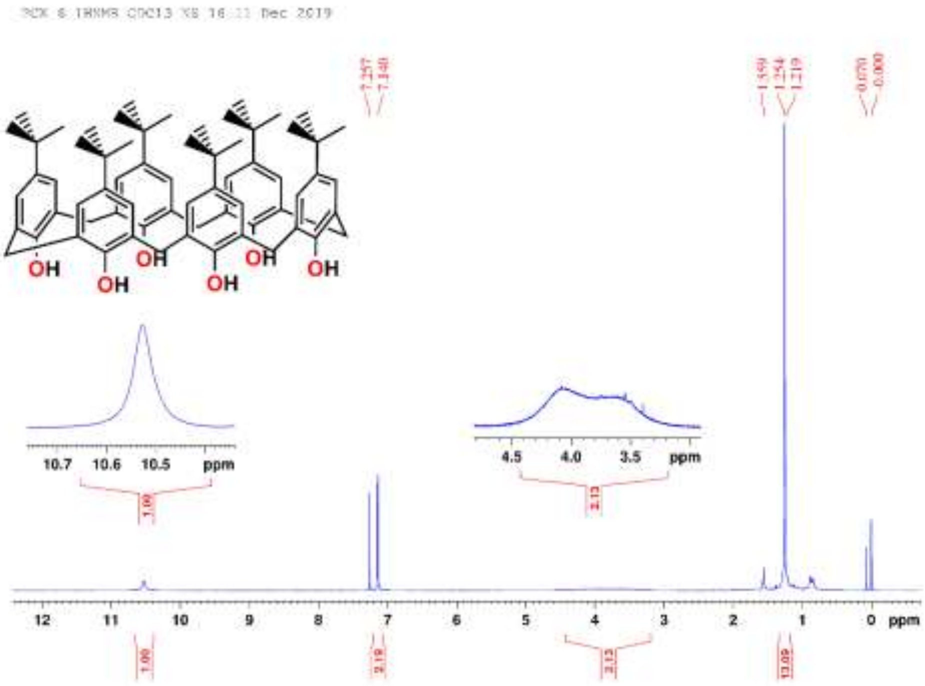


Figure S5. Showing CX[6] ^{1}HNMR (500 MHz, $CDCl_3$: ^{1}H NMR ($CDCl_3$) δ: 1.25 (s, 54 H), 3.69 (s, 12 H), 7.14 (s, 12 H), 10.533 (s, 6 H). Locked in $CDCl_3$.

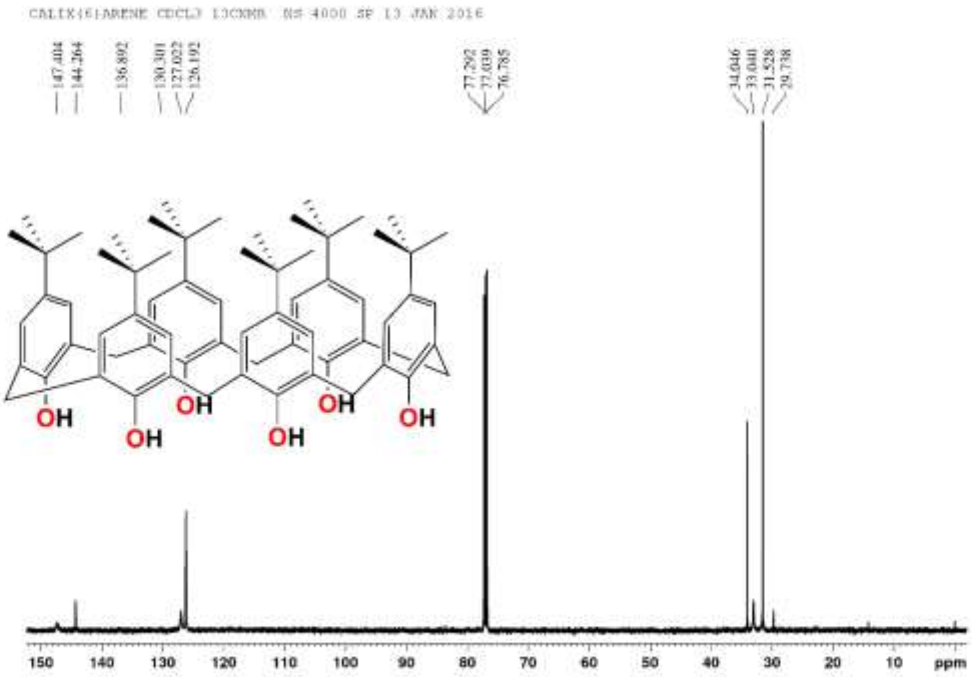


Figure S6. Showing CX[6] ^{1}HNMR (500 MHz, $CDCl_3$: ^{13}CNMR ($CDCl_3$).

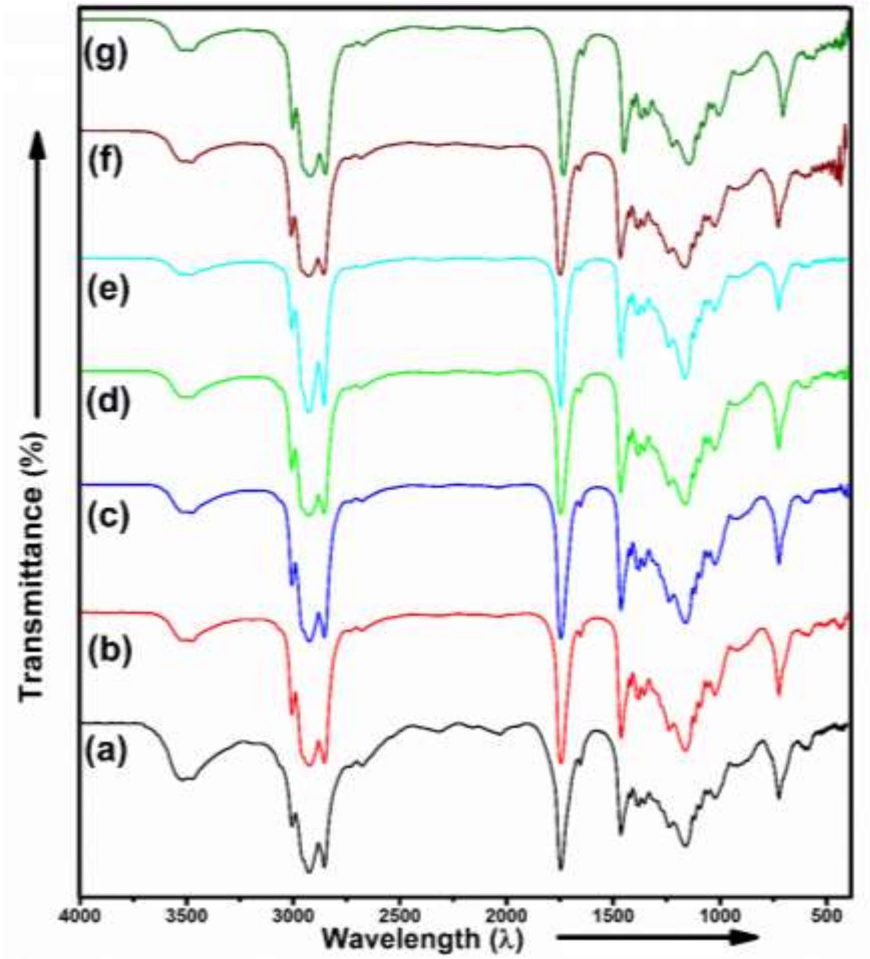


Figure S7. Showing Oxidation Stability by FTIR with neat PLBO and PLBO spiked with various concentrations of CB[6] and CX[6] before oxidation (a) Blank PLBO, (b) CB[6] 1000 ppm, (c) CB[6] 2000 ppm, (d) CB[6] 3000 ppm, (e) CX[6] 1000 ppm, (f) CX[6] 2000 ppm, (g) CX[6] 3000 ppm.

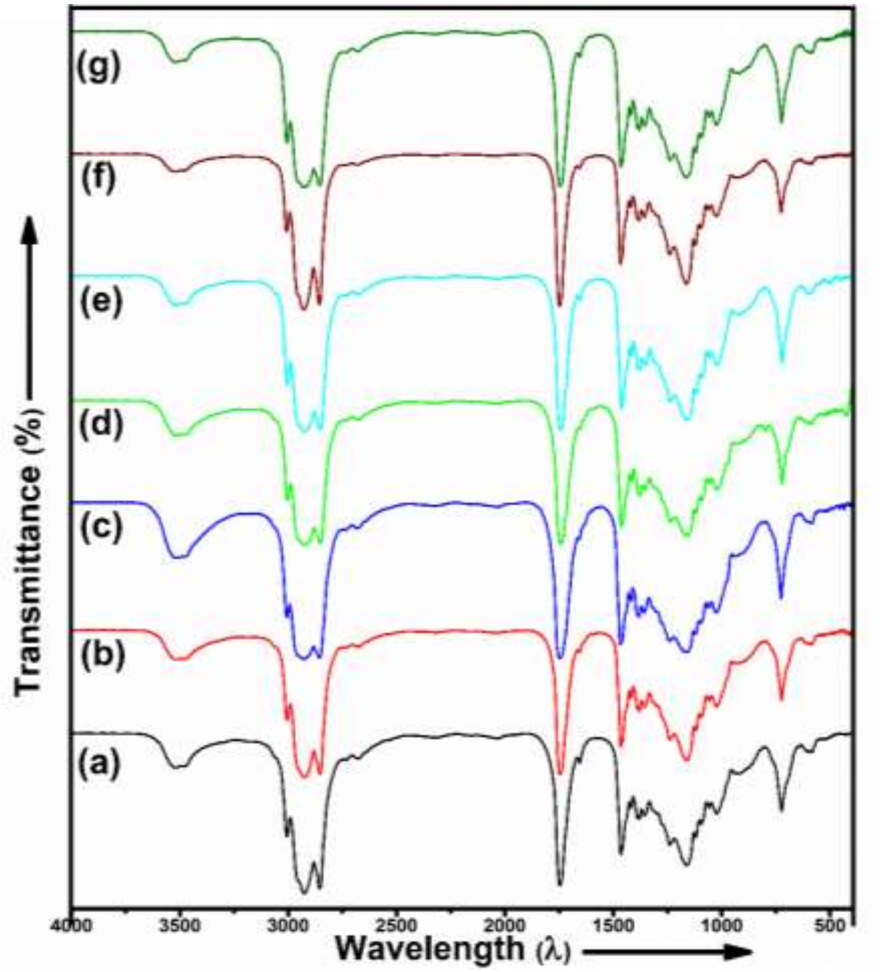


Figure. S8. Showing Oxidation Stability by FTIR with neat PLBO and PLBO spiked with various concentrations of CB[6] and CX[6] after Oxidation (a) Blank PLBO, (b) CB[6] 1000 ppm, (c) CB[6] 2000 ppm, (d) CB[6] 3000 ppm, (e) CX[6] 1000 ppm, (f) CX[6] 2000 ppm, (g) CX[6] 3000 ppm.

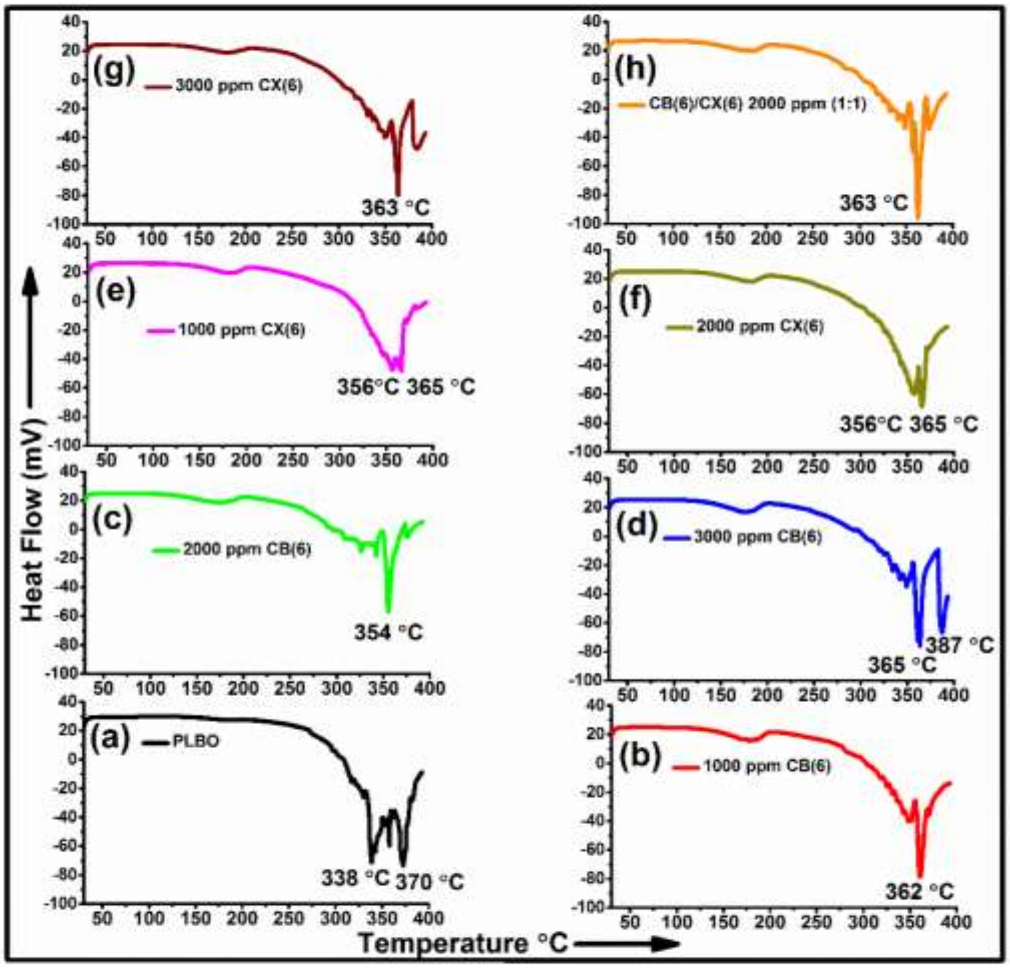


Figure S9. Showing Oxidation Stability by DSC with neat PLBO and PLBO spiked with various concentrations of CB[6] and CX[6]. (a) Blank PLBO, (b) CB[6] 1000 ppm, (c) CB[6] 2000 ppm, (d) CB[6] 3000 ppm, (e) CX[6] 1000 ppm, (f) CX[6] 2000 ppm, (g) CX[6] 3000 ppm (h) CB[6]/CX[6] 2000 ppm (1:1).

Antioxidant activity of PLBO and blends of synthesized compounds in PLBO was determined with differential scanning calorimeter (DSC) according to ASTM E 2009-08. DSC analyses were conducted on Perkin Elmer STA 4000 thermal analyzer under oxygen atmosphere from 30 to 400 °C.

Table S1. Showing Worn Surface Analysis of Steel balls, analyzed by EDX.

S.No.	Elements	Percent %	PLBO	CB[6] 1000 ppm	CB[6] 2000 ppm	CB[6] 3000 ppm	CX[6] 1000 ppm	CX[6] 2000 ppm	CX[6] 3000 ppm
1	C	Weight	51.55/51.63 /55.37/50.61	26.00/27.30/26.19	24.68/24.78	24.54	95.34/63.62 /65.39	81.35/73.07 /97.68	76.25/81.28 /81.13
2	N	Weight		47.81/31.69/40.86	54.60/49.11	34.03			
3	O	Weight	1.86/2.47 /3.67/5.20	13.76/14.92/11.56	19.48/16.09	13.10	-1.94/0.05 /0.35	7.36/-6.93 /-2.06	5.59/2.93 /0.55
4	Cr	Weight	0.60/1.13 /0.53/1.24	0.16/0.68/0.56	0.07/0.30	0.58	0.29/0.34 /33.85	-0.16/0.79 /0.01	0.64/-0.03 /-0.34
5	Fe	Weight	45.99/44.77 /40.44/42.95	12.27/25.41 /20.83	1.17/9.72	27.75	6.31/35.99 /33.85	11.45/33.08 /4.37	17.52/15.82 /18.66
6	C	Atomic	81.86/81.47 /82.71/79.03	32.49/38.30/35.15	28.57/30.54	35.23	100.03/89.01 /89.54	91.09/97.22 /100.62	90.38/93.56 /94.91
7	N	Atomic		51.25/38.11/47.02	54.20/51.91	41.89			
8	O	Atomic	2.21/2.93 /4.12/6.10	12.92/15.71/11.64	16.92/14.89	14.12	-1.53/0.05 /0.36	6.19/-6.93 /-1.59	4.98/2.53 /0.49
9	Cr	Atomic	0.22/0.41 /0.18/0.45	0.16/0.22/0.17	0.02/0.09	0.19	1.42/10.83 /0.13	-0.04/0.24 /0.00	0.18/-0.01 /-0.09
10	Fe	Atomic	15.71/15.19 /12.99/14.42	3.30/7.67/6.01	0.29/2.58	8.57	0.07/0.11 /9.97	2.76/9.47 /0.97	4.47/3.92 /4.69

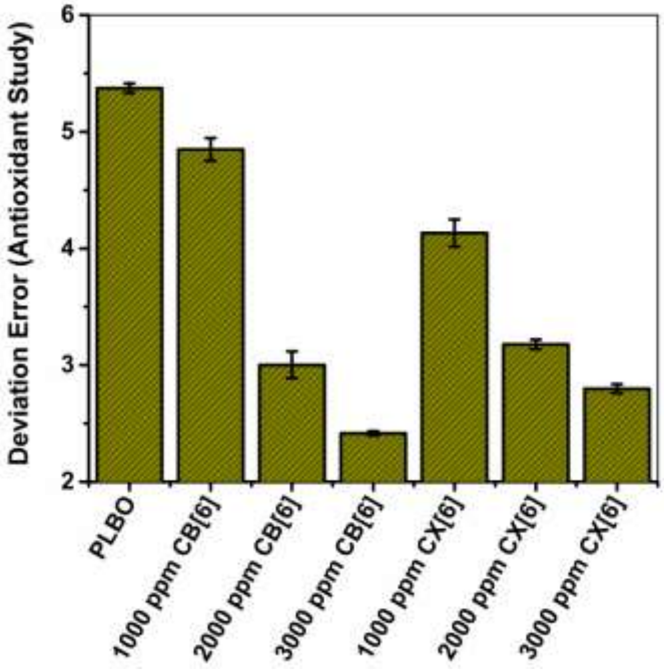


Figure S10. Showing mean and standard deviation for repetitive experiments of AO (Antioxidant Total Oxidation Products Study via IP 306 oxidation test and ASTM standard D974).

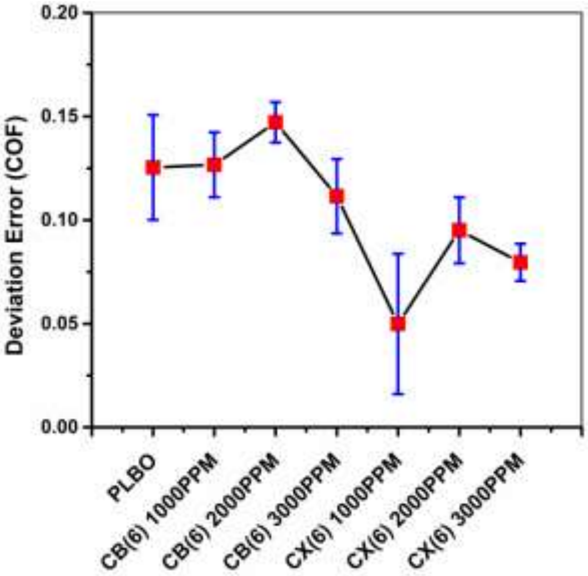
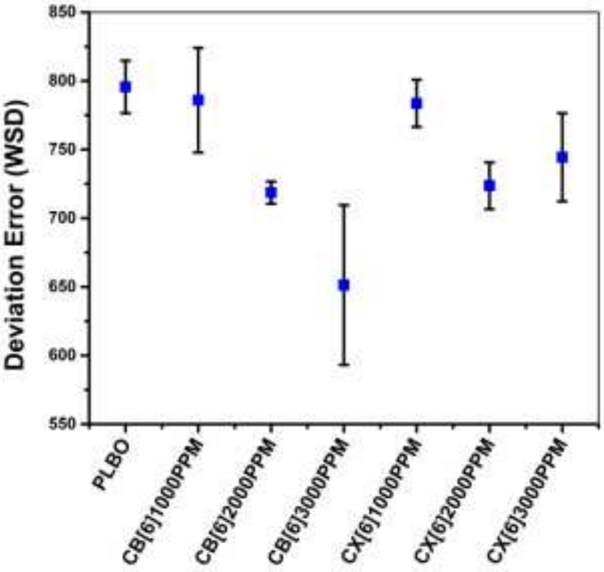


Figure S11. Showing mean and standard deviation for repetitive experiments of COF (Coefficient of Friction Four ball test ASTM D4172).

Figure S12. Showing mean and standard deviation for repetitive experiments of WSD (Wear Scar Diameter Four ball test ASTM D4172).



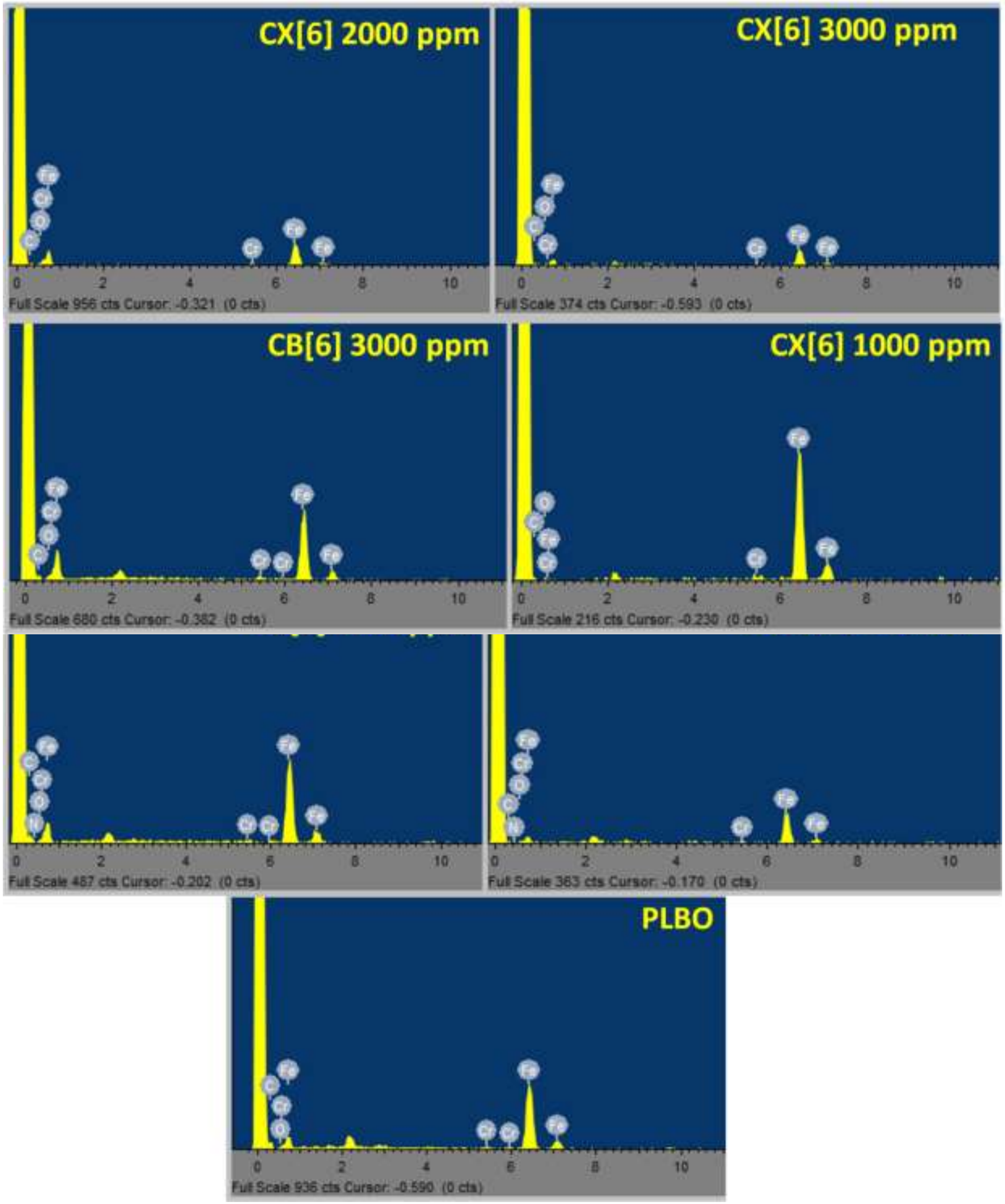


Figure S13. EDAX Elemental Analysis of Worn Surface

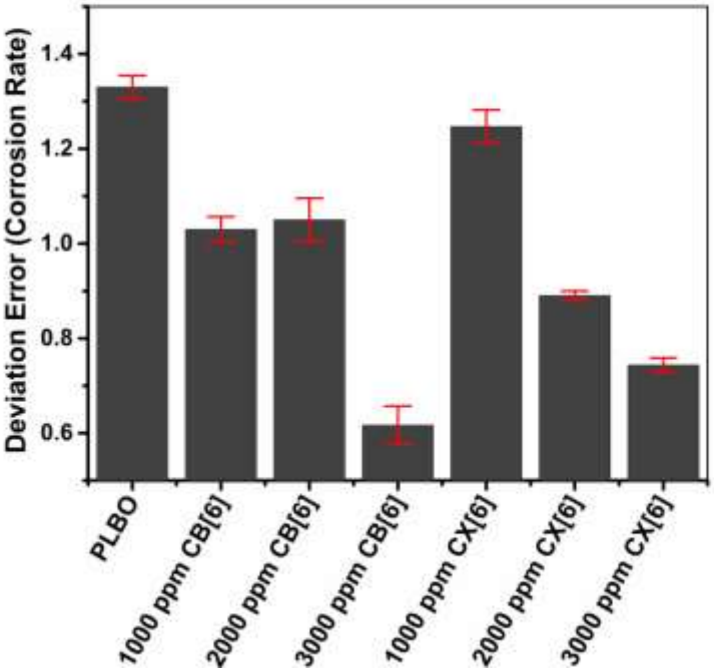


Figure S14. Showing mean and standard deviation for repetitive experiments of AC (Anticorrosion Study Four ball test ASTM D4172).

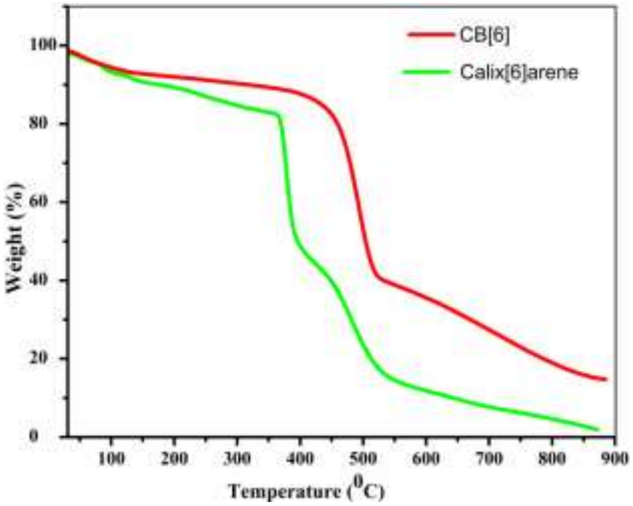


Figure S15. TGA curve of CB[6] and CX[6] showing their high-temperature stability