

Electronic Supplementary Information (ESI†)

Spirobifluorene-BINOL-based Microporous Polymer Nanoreactor for Efficient 1*H*-Tetrazole Synthesis and Iodine Adsorption with Facile Charge Transfer

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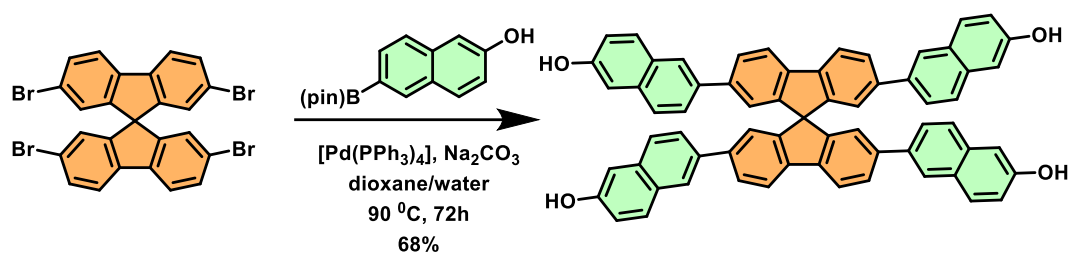
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1. Experimental Section.

1.1. Materials and Methods. All the reagents, starting materials, and solvents purchased from commercial suppliers and were used without further purification. Solvents were dried as per literature procedure prior to use according to the requirements. Thin layer chromatography (TLC) on silica gel GF₂₅₄ was used for the determination of R_f values, and the visualization was performed by irradiation with UV lamp at 254 nm. Column chromatography was performed on Merck silica gel (100-200 mesh) with eluent as mentioned. ¹H (500 MHz) and ¹³C (125 MHz) NMR spectra were recorded in a Bruker Advance III HD spectrometer in deuterated solvent at ambient temperature (300 K). Chemical shifts are reported in ppm (δ) relative to tetramethylsilane (TMS) as the internal standard (DMSO-d₆ δ 3.6 and 2.6 ppm for ¹H and 39.0 ppm for ¹³C). Solid state ¹³C CPMAS NMR spectra were recorded in a Bruker Ultrashield Plus-500 NMR spectrometer. Mass spectra were recorded on Agilent 6500 Series Q-TOF spectrometer. Fourier transform infrared spectra (FTIR, 4000-600 cm⁻¹) were performed on a Nicolet 6700 FT-IR spectrometer (Thermo Fischer) instrument, the wave numbers of recorded IR-signals are reported in cm⁻¹. Elemental analyses were carried out using a Perkin-Elmer Series-II. Thermogravimetric analyses (TGA) were performed on a Pyris Diamond Tg Dta (PerkinElmer) instrument. The Phosphate based porous organic polymers were observed under scanning electron microscope (SEM) model ZEISS SUPRA 40. The samples were prepared on Al stubs by adding powder polymers mounting on top of double-sided tapes. TEM measurements were carried out in a FEI Tecnai G2 20 TWIN machine operating at an accelerating voltage of 200 V. TEM samples were prepared by mounting on the carbon coated copper grid for analysis. The particle size distribution histogram was obtained with imageJ software X-Ray diffraction patterns of the powder organic polymer samples were obtained using a Rayon X diffractometer using Cu-K α (0.15406 nm) radiation. The N₂ adsorption/desorption isotherms of the sample was recorded on a Micromeritics 3-Flex Surface Characterization Analyzer at 77 K. XPS of the samples were recorded on PHI 5000 VersaProbe III, ULVAC-PHI, INC.

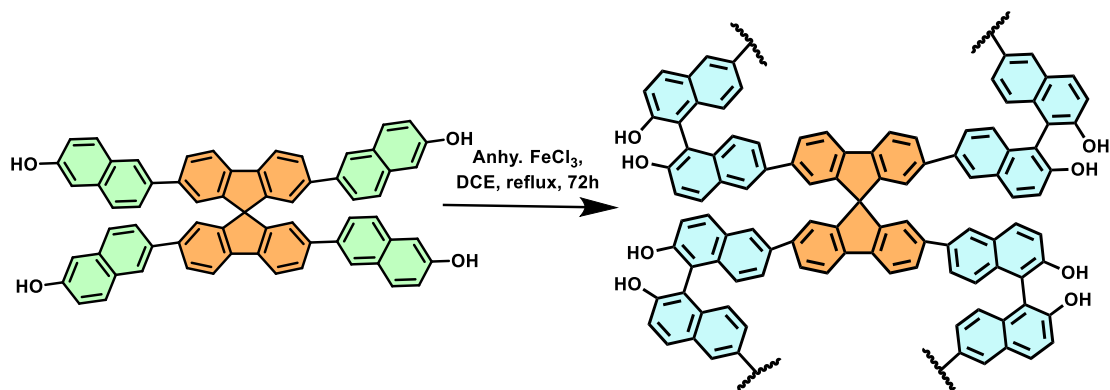
1.2. Synthetic Procedures

1.2.1. Procedure for synthesis of Monomer 1: 2,2',7,7'-tetrabromo-9,9'spirobifluorene (120 mg, 0.19 mmol) along with boronic ester of 6-bromo-2-naphthol (450 mg, 1.14 mmol), Pd(PPh₃)₄ (5 mol%, 17 mg) in dioxane/H₂O (3:1) was stirred at 90 °C under argon for 48 h. Then, the reaction mixture was allowed to cool to room temperature, quenched with water and extracted with ethyl acetate. The organic layer was washed with brine, dried over Na₂SO₄ and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (chloroform/methanol = 20:1) to afford the compound **1** as brown solid (68% yield). ¹H NMR: (DMSO-d₆, 500 MHz, ppm) 9.76 (1H, s); 8.26 (1H, d); 7.91-7.94 (2H, m); 7.75 (1H, d); 7.63 (1H, d); 7.53 (1H, d); 7.08 (1H, s); 7.00-7.05 (2H, m). ¹³C NMR (DMSO-d₆, 125 MHz, ppm): 156.5, 150, 140, 134, 129, 126.26, 125.93, 125.57, 124.93, 122.99, 118.09, 108.51, 73. FT-IR (KBr pellet, cm⁻¹): 3496, 2963, 1562, 1271, 1104. MALDI-TOF: (M+H⁺) 885.2961 (calc.); 885.0285 (obs.).



Scheme S1. Synthesis of monomer **1**.

1.2.2. Procedure for the Synthesis of Polymer SBF-BINOL-6: Monomer **1** (100 mg, 1 eqv.) dissolved in anhy. dichloroethane in presence of anhy. FeCl_3 (129 mg, 7 eqv.) was refluxed for 3 days. Then, the resulting precipitate was filtered and washed with dil. HCl and MeOH several times. The precipitate was again washed with CHCl_3 , acetone and MeOH for 48 h under Soxhlet extraction. Finally, it was dried under vacuum and the yellow polymer **SBF-BINOL-6** was obtained with 81% yield. Solid state ^{13}C CP/MAS NMR (ppm). 67, 108, 113-116, 123-129, 137-141, 152. FT-IR (KBr pellet, cm^{-1}). 3425, 2935, 1559, 1284, 1091. TGA. 5% weight loss at 372 °C.



Scheme S2. Synthesis of polymer **SBF-BINOL-6**.

1.2.3. Procedure for the *in situ* Synthesis of Ag Nanoparticle Loaded Polymer Catalyst (Ag@SBF6): Aqueous solution of AgNO_3 (3 mL, 10 mM) was added dropwise to a well-dispersed suspension of **SBF-BINOL-6** (10 mg) in a mixture of 5 mL of distilled water and 5 mL of methanol and stirred for 1 h. Following that, freshly prepared methanolic solution of NaBH_4 (3 mL, 10 mM) was added dropwise into the aforementioned mixture and continued stirring for another 2 h. The overall mixture was turned black indicating the formation of Ag nanoparticle loaded **SBF-BINOL-6**. The mixture was centrifuged at 5000 rpm and washed with methanol for several times. After centrifugation, solid product was dried under vacuum at 80 °C.

1.2.4. General Process of [3+2] dipolar cycloaddition by Ag@SBF6: Benzonitrile (1 mmol) and NaN₃ (1 mmol) were added to 3 mL of DMF. To this mixture, 5 mg of Ag@SBF6 was added and the resultant mixture was stirred at 120 °C for 24 h. After completion of the reaction, the solvent was removed entirely under vacuum. Then the product was extracted with ethyl acetate with prior acidification with 2N HCl and washed repeatedly with water. The product was then precipitated from CHCl₃/hexane and subjected to NMR.

1.2.5. General Process of iodine adsorption by SBF-BINOL-6 and Ag@SBF6: The gravimetric technique was used to determine the iodine adsorption over the BINOL based POPs at various time intervals. POP (30 mg) was added into a 5 mL open vial and the vial was placed into a large sealed vial (30 mL) containing excess amount of solid iodine. The entire system was kept in an oven set to 75 °C for a certain amount of time. After the iodine-adsorbed sample was cooled to room temperature, it was weighed.

1.2.6. General procedure for electrochemical measurements: The Nyquist plot was obtained using the electrochemical impedance spectroscopy (EIS) technique, measured within the 100-1000 Hz frequency range at E= 0 V_{Ag/AgCl} using DC voltage with an introduction of 1.2 V under illuminated conditions in a CHI 6600C instrument.

1.2.7. General Process of recycling for SBF-BINOL-6: After complete saturation through iodine vapor uptake, the polymer was washed with vigorous stirring for 4 h in presence of ethanol and was filtered through simple gravity filtration technique. Thereafter, it was put through next run with prior vacuum drying.

1.2.8. Theoretical Calculations: All the theoretical calculations were performed with GAUSSIAN 16 program under DFT/B3LYP/DGTZVP basis set. The binding energy results were obtained with the following equation.

$$\Delta E = E_{host-guest} - (E_{host} + E_{guest})$$

1.2.9. Calculations for conductivity: The conductivity value (σ) was obtained using the following equation.

$$\sigma = (1/R) \times \text{cell constant} = (1/R) \times L/A$$

where R represented the resistance in ohm and cell constant is calculated in cm⁻¹.

2. Characterization

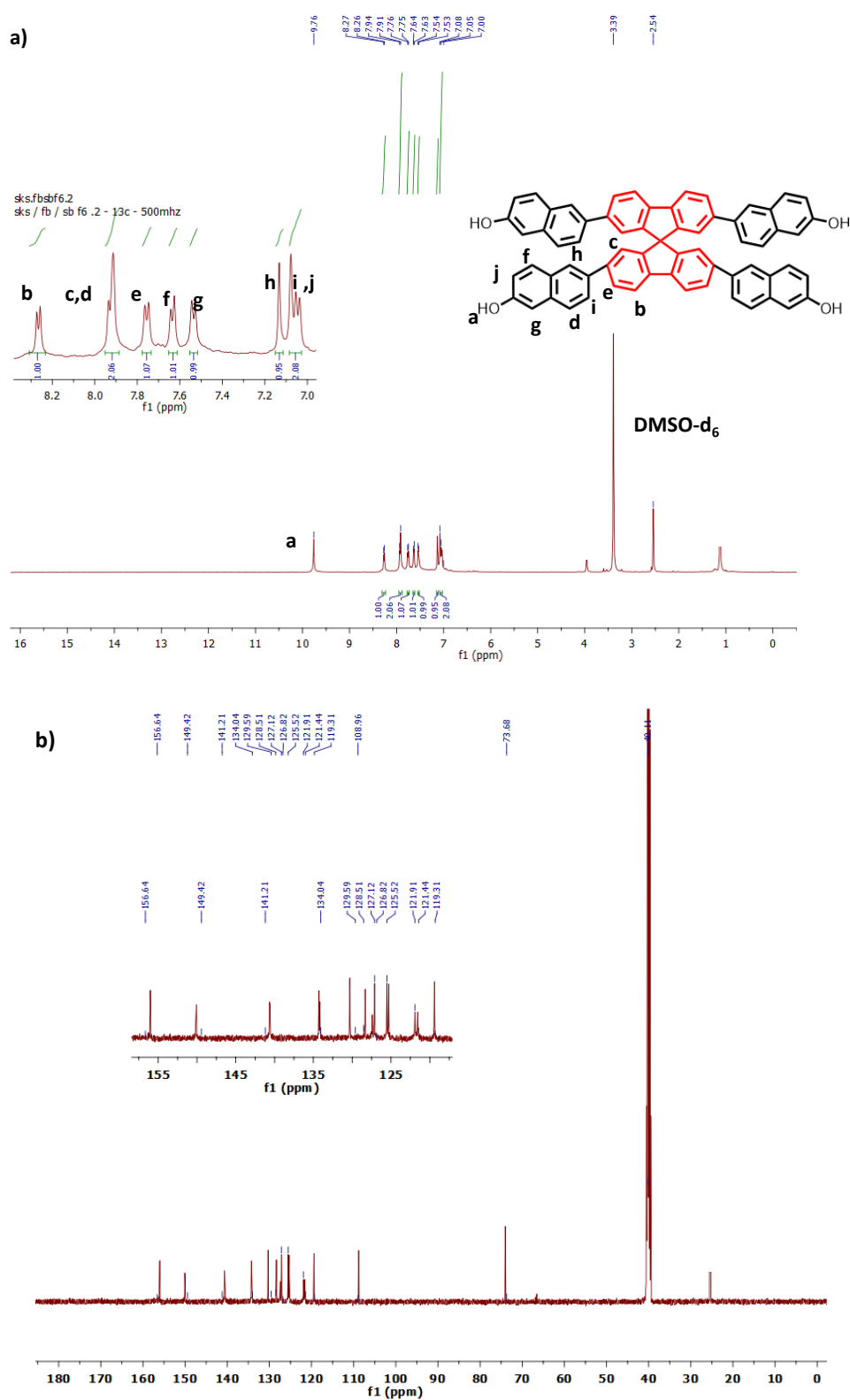


Fig. S1. a) ^1H and b) ^{13}C NMR spectra for monomer **1** in DMSO-d_6 .

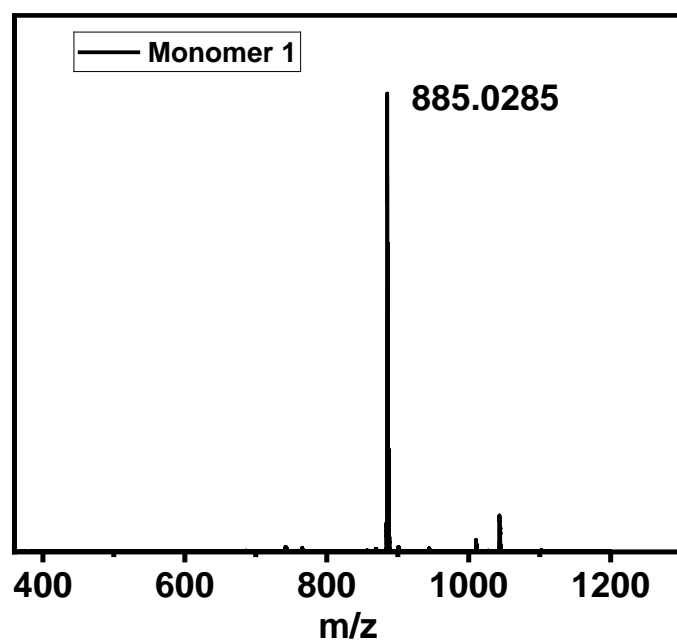


Fig. S2. MALDI-TOF mass spectra for **monomer 1**.

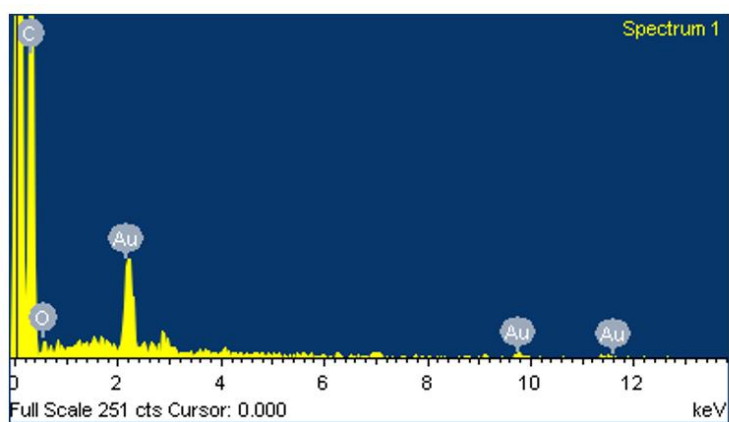


Fig. S3. EDAX pattern for **SBF-BINOL-6**.

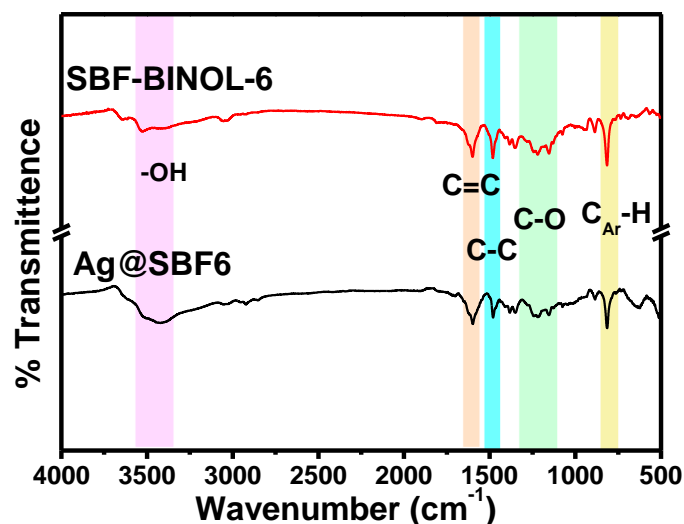


Fig. S4. FT-IR spectra (KBr pellets) of Ag@SBF6 and SBF-BINOL-6.

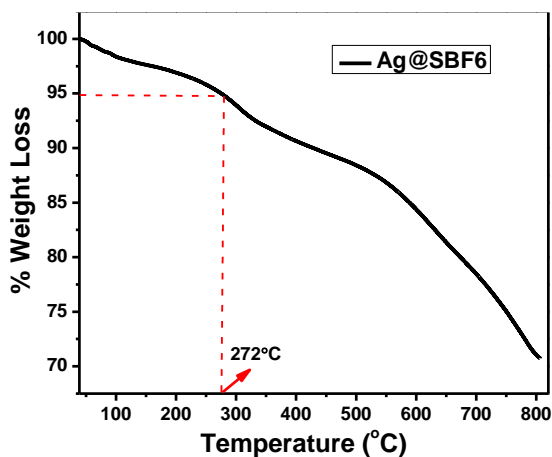


Fig. S5. TGA curve of the Ag@SBF6 under argon atmosphere.

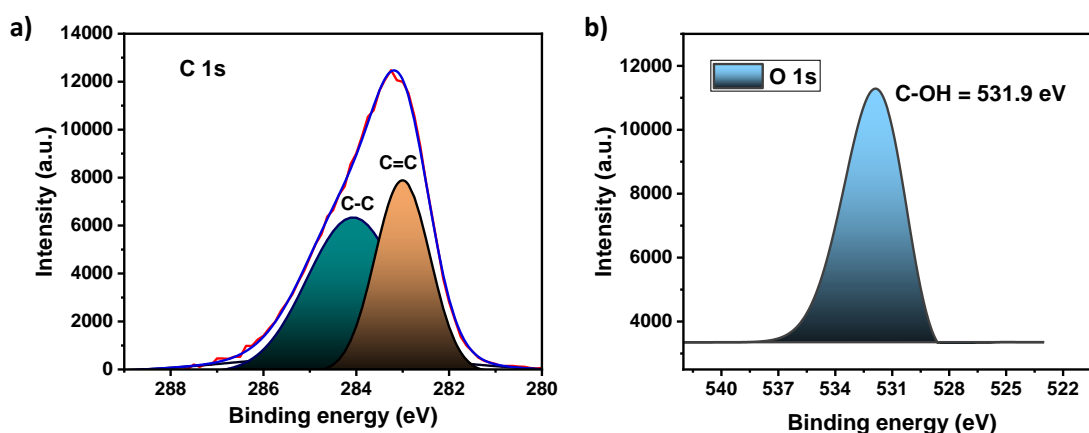


Fig. S6. Deconvoluted X-ray photoelectron spectroscopy (XPS) pattern for Ag@SBF6. The binding energy plots of (a) C 1s, (b) O 1s.

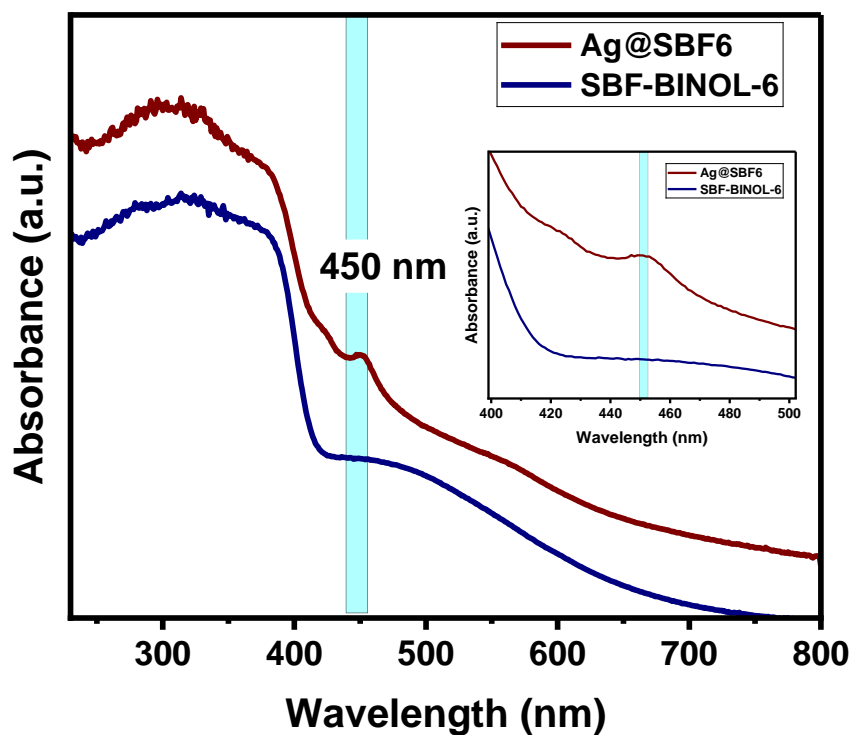


Fig. S7. UV-DRS spectra for **SBF-BINOL-6** and **Ag@SBF6**.

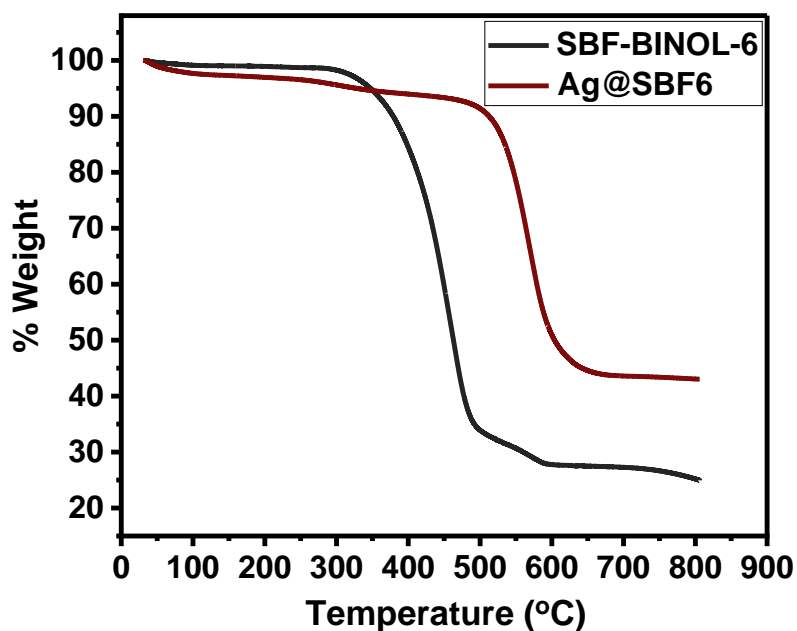


Fig. S8. TGA profile for **SBF-BINOL-6** and **Ag@SBF6** under air with flow rate of 100 mL/min. Temperature was increased with a heating rate of 10 °C/min. Both the cases, 5 mg of the polymer was taken for analysis. Total % loading of silver nanoparticles was analyzed from % weight loss which appeared to be 18.12%.

Table S1. Table for solvent optimization for synthesis of 1*H*-tetrazole.

Entry	Solvent	Temperature (°C)	%Yield
1	MeCN	80	25
2	CHCl ₃	62	trace
3	Water	100	10
4	THF	64	trace
5	DMSO	120	60
6	DMF	120	99

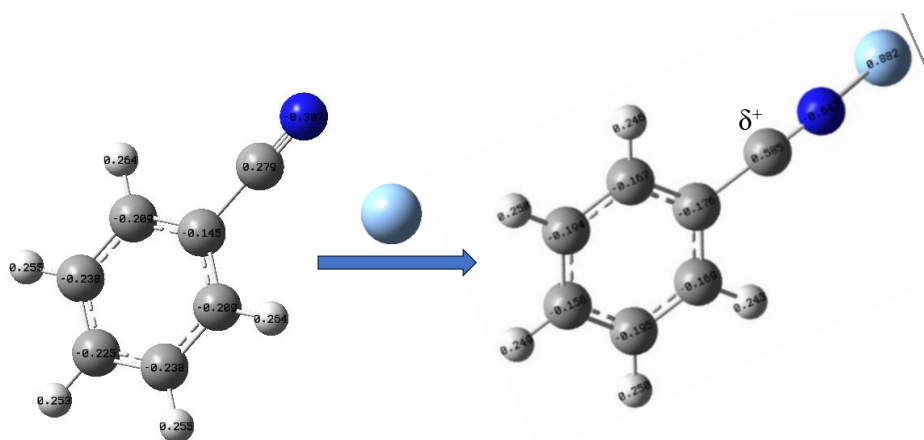


Fig. S9. DFT based NBO charges calculation of activation of benzonitrile -CN moiety by **Ag@SBF6**. (δ^+ value for -CN carbon atom is changed from 0.279 to 0.585)

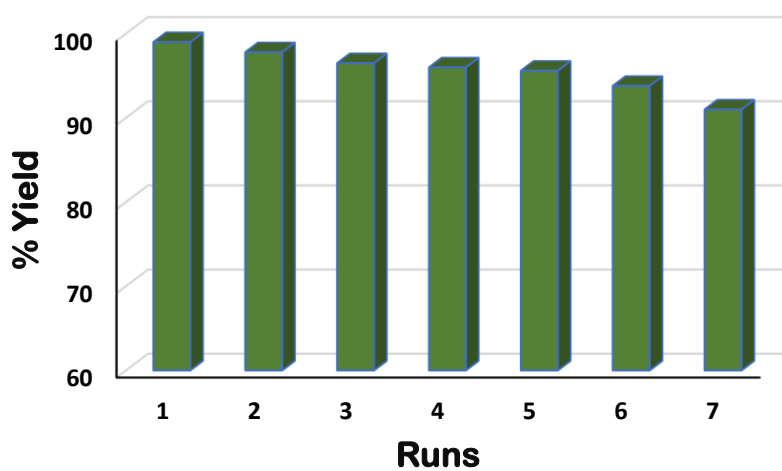


Fig. S10. Recyclability profile for **Ag@SBF6** up to 7th cycle of tetrazole synthesis.

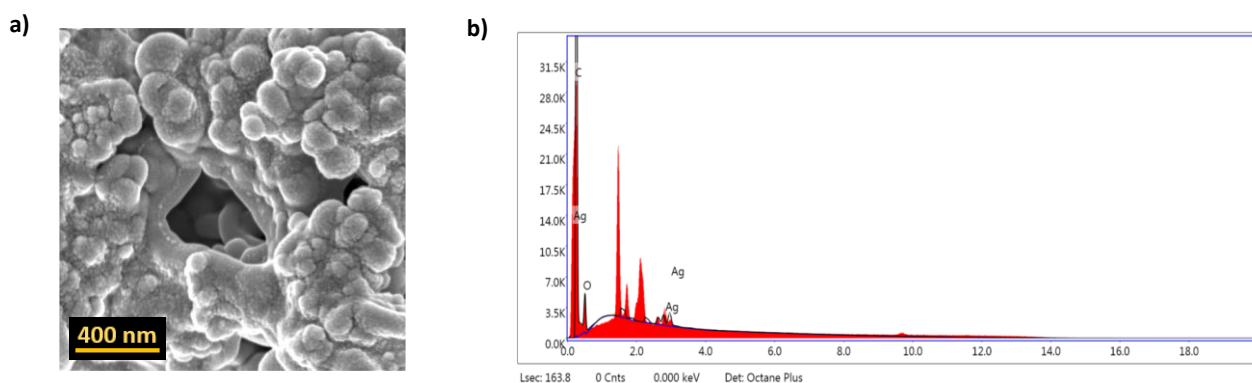


Fig. S11. (a) SEM image of **Ag@SBF6** after recycling for 7th cycle in the formation of tetrazole. (b) EDAX pattern.

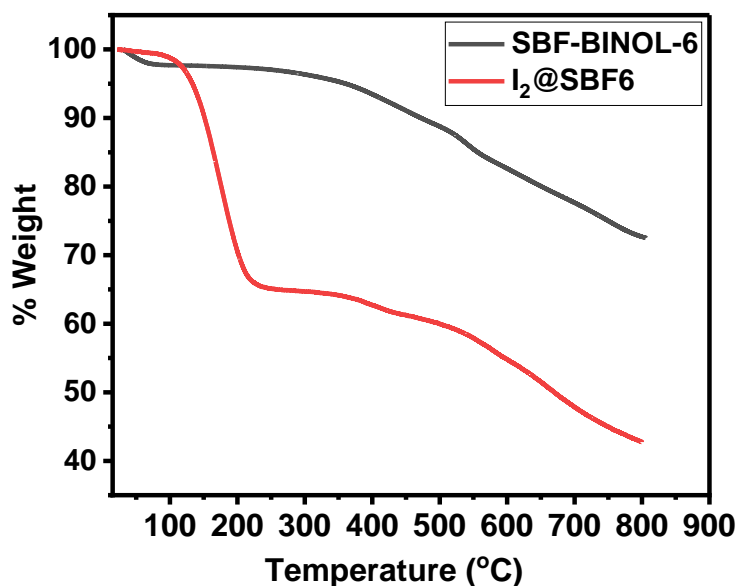


Figure S12. TGA profile under argon atmosphere for **SBF-BINOL-6** and **I₂@SBF6** within the temperature range 30-800 °C with increase rate of 10 °C/min. The polymer amount taken was 9.012 mg for the analysis. %Weight loss was calculated to be 81% and 42% for **SBF-BINOL-6** and **Ag@SBF6** respectively.

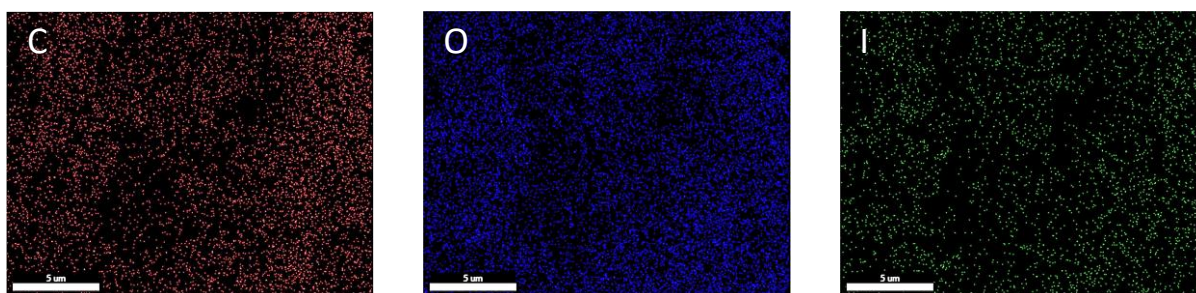


Figure S13. Elemental mapping from EDAX over iodine loaded **SBF-BINOL-6**.

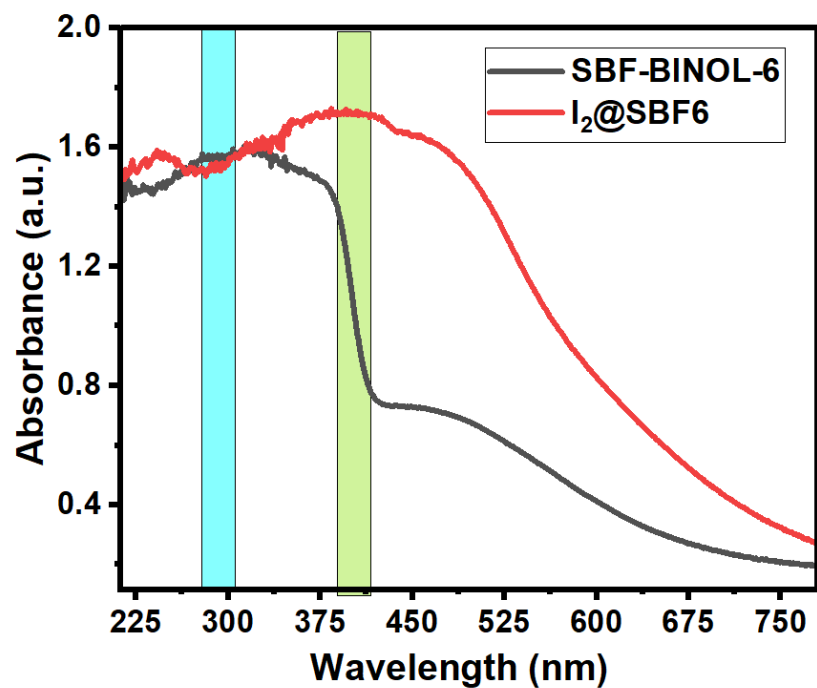


Figure S14. UV-DRS patten for both SBF-BINOL-6 and I₂@SBF6.

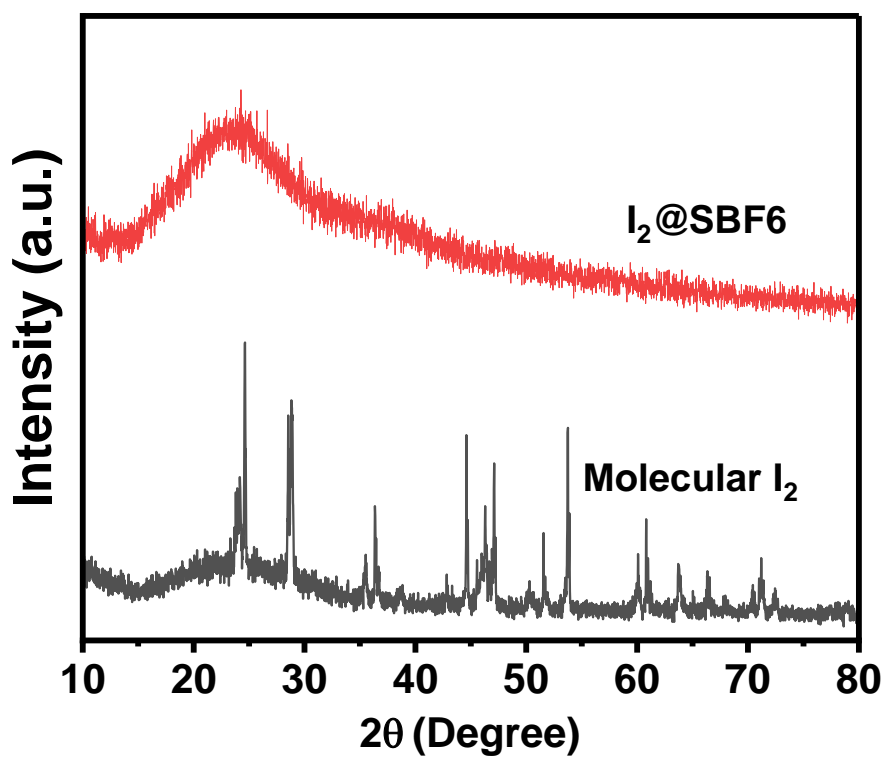


Figure S15. PXRD pattern for I₂@SBF6 (red) and molecular iodine (black).

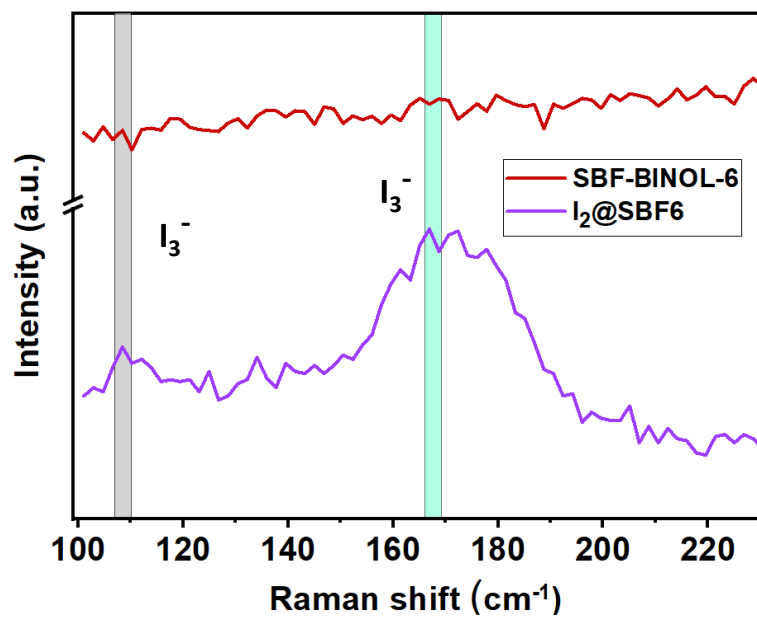


Figure S16. Raman spectra for iodine loaded polymer **I₂@SBF6** and **SBF-BINOL-6**.

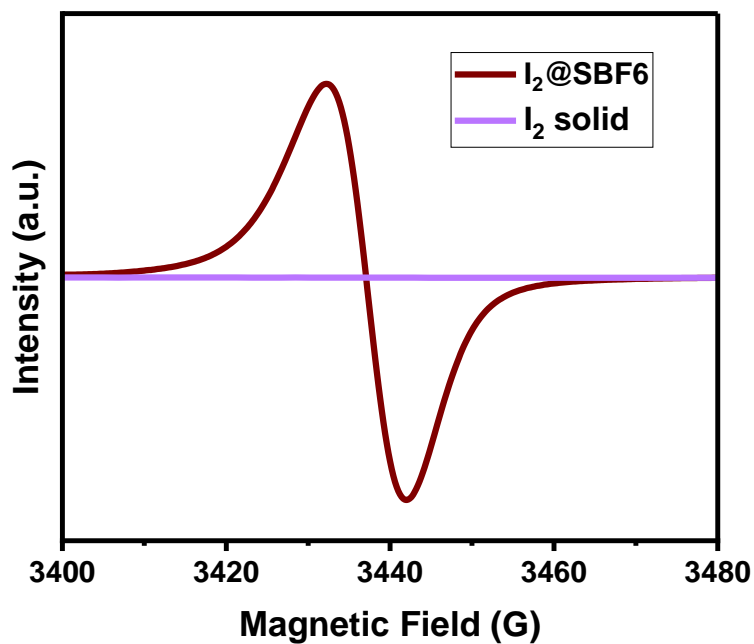


Figure S17. EPR spectra for iodine loaded polymer **I₂@SBF6** and solid iodine.

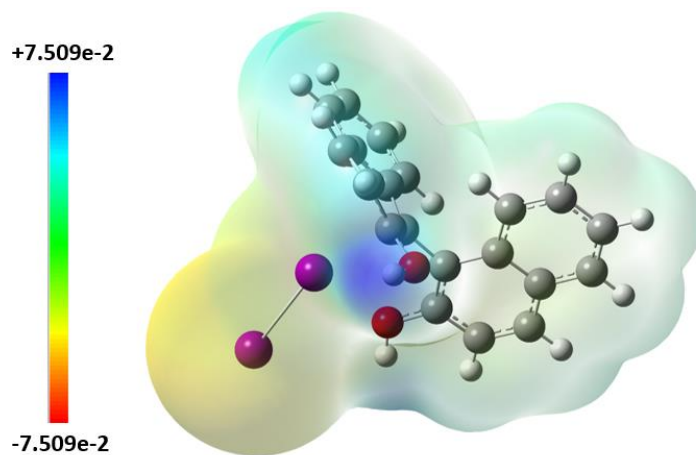


Figure S18. ESP mapping for host-guest complex of BINOL unit and iodine.

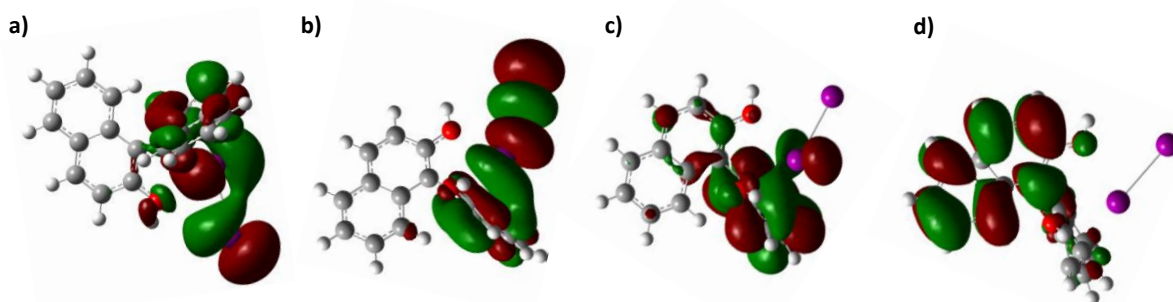


Figure S19. Electronic distribution for a) HOMO; b) LUMO; c) LUMO+1 and d) LUMO+2 for host-guest complex of BINOL unit and iodine.

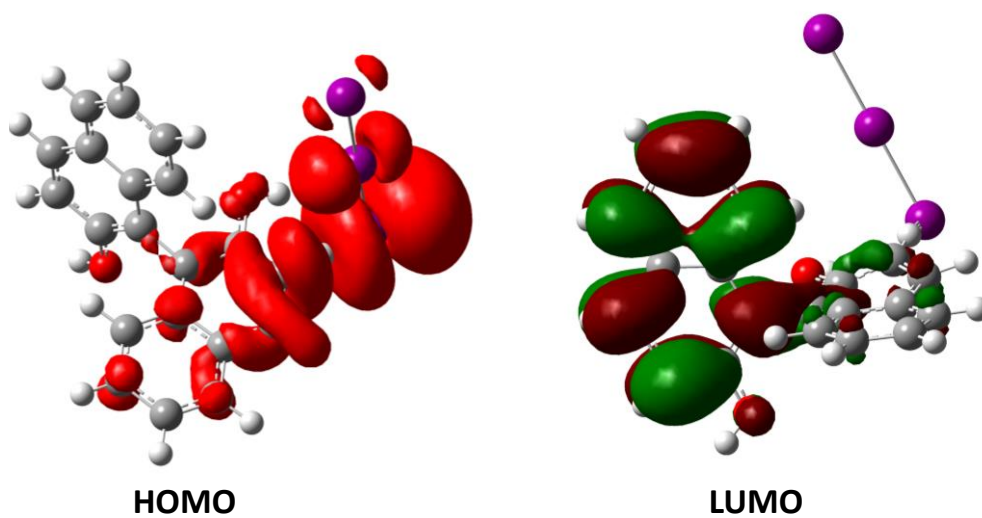


Figure S20. Electronic distribution for HOMO and LUMO of BINOL model unit and triiodide.

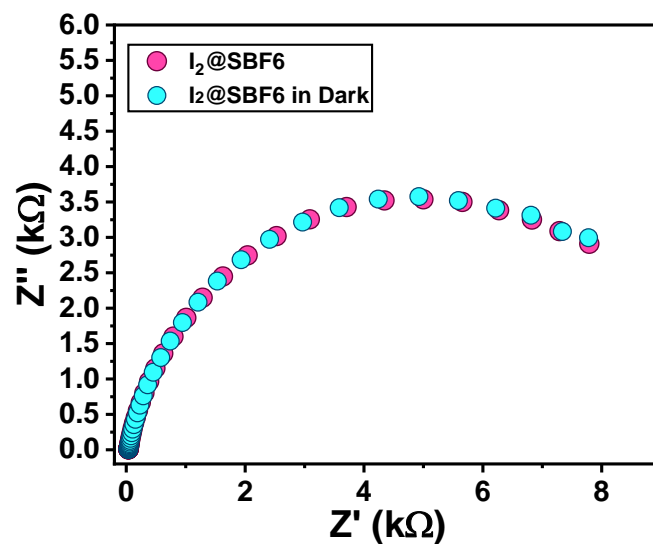


Figure S21. Nyquist plot for **I₂@SBF6** under dark and illuminated condition at starting voltage of 1.2 V.

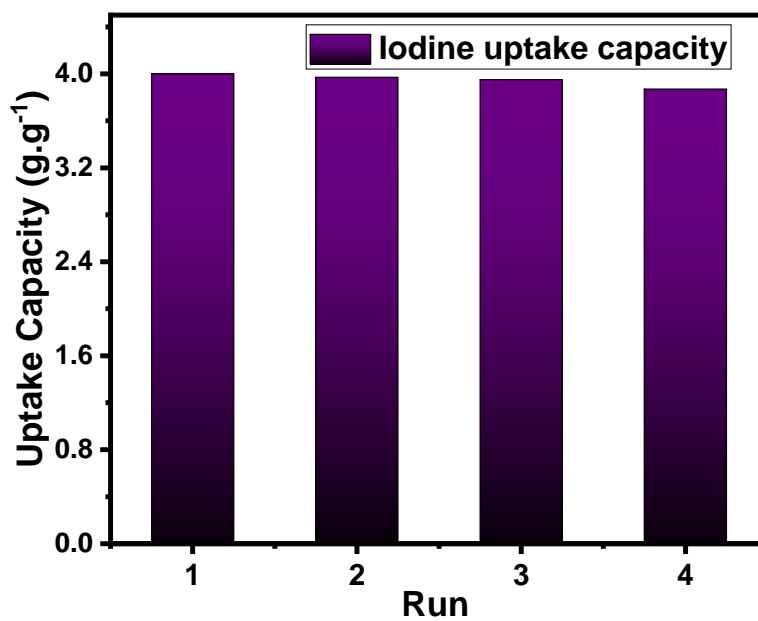


Figure S22. Recyclability profile for **SBF-BINOL-6** after iodine adsorption in vapor phase.

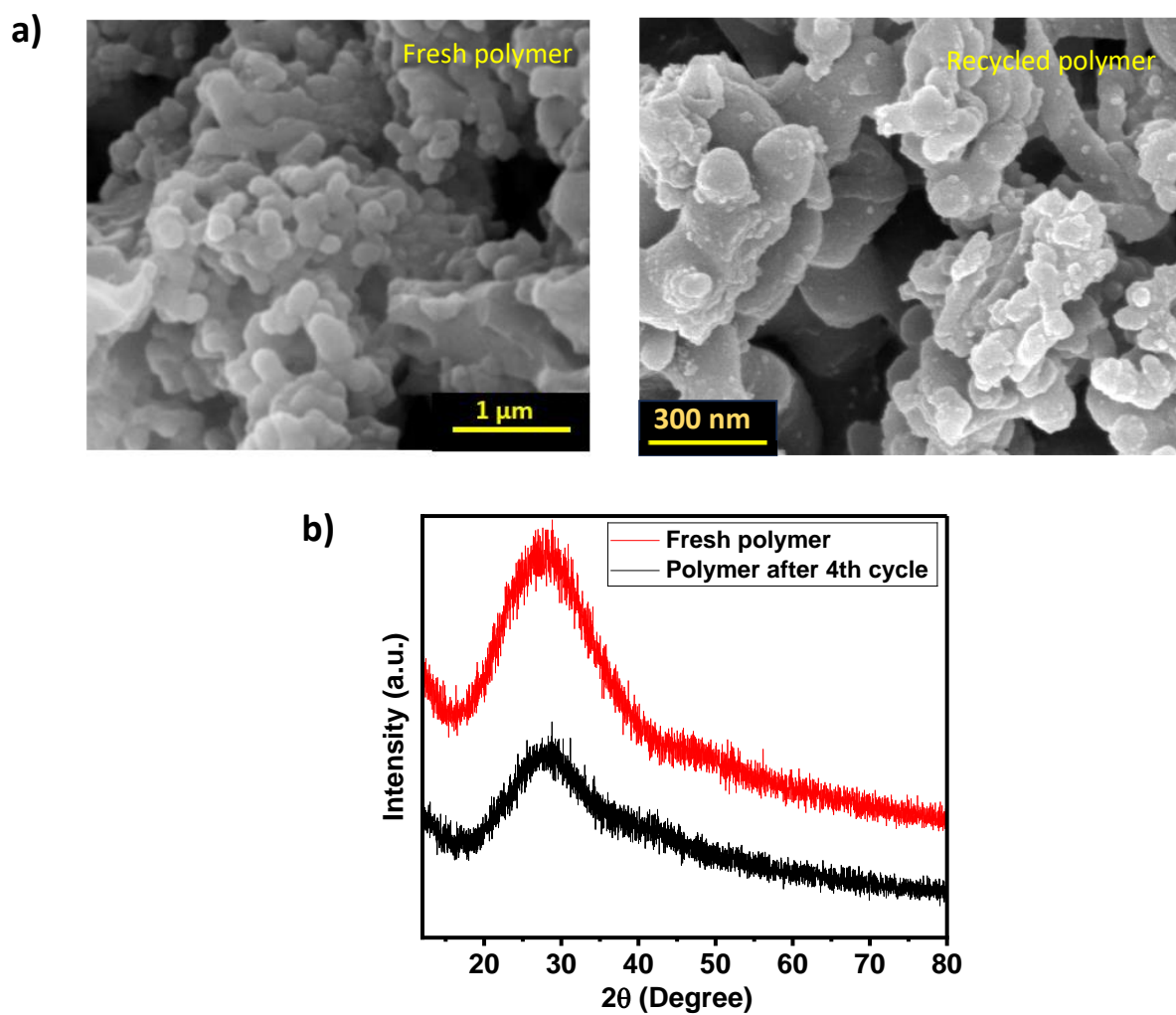


Figure S23. a) SEM images and b) PXRD pattern for fresh and recycled **SBF-BINOL-6** after iodine adsorption in vapor phase.