Electronic supplementary information

Azine- and Imine-linked Conjugated PolyHIPEs through

Schiff-Base Condensation Reaction

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Chemicals

Chemicals: Terephthalaldehyde (99 %, Sigma-Aldrich), hydrazine monohydrate (98 %, Sigma-Aldrich), Pluronic F-127 (Sigma), silicon oil (99 %, Sigma-Aldrich), and paraffin oil (99 %, Sigma-Aldrich); and solvents: petroleum benzene (boiling range 100-140 °C, Merck), dimethylformamide (\geq 99.8 %, Sigma-Aldrich), and ethanol (absolute, Sigma-Aldrich) were all used as received.

Methods

NMR spectroscopy analyses were performed on a Bruker Avanze 400 MHz spectrometer. ¹H NMR spectra were carried out at room temperature in the pulse Fourier-transform mode using various deuterated solvents such as CDCl₃, DMSO- d_6 all purchased from Cambridge Isotope Laboratories. The relaxation delay was set to 5 s in order to guarantee complete proton relaxation. In case of ¹³C CP/MAS NMR spectroscopy, the 4 mm CP-MAS probe with ¹H-¹⁹F and ³¹P-¹⁵N coils and maximum spinning rate of 16 kHz with a delay time of 2 s was used. Chemical shifts are given in ppm relative to a SiMe₄ standard. NMR data were processed using MestReNova software.

FTIR spectroscopy measurements were performed on the dried grinded samples using a Perkin-Elmer (Inc., Waltham, MA, USA) FTIR spectrometer with attenuated total reflection (ATR) in a 400-4000 cm⁻¹ range at a resolution of 4 cm⁻¹. The presented spectra are an average of 32 consecutive measurements on Ge-crystal.

Scanning electron microscopy (SEM) images were collected on a JWS-7515, JEOL scanning electron microscope. The samples were attached to a carbon tab for better conductivity and afterwards a thin layer of Pt was sputtered on a samples' surface prior to scanning analysis (for SEM investigations). SEM micrographs were taken at a magnification of 5000-times, at 7 mm working distance and 20 kV voltage applied.

Nitrogen physisorption analysis was carried out by determining adsorption and desorption isotherms of N₂ at -196 °C using a Micromeritics TriStar II 3020 instrument. Prior to characterization, the samples were degassed under N₂ stream (purity 6.0) using a programmed bilevel heating, with the first heating stage at 90 °C for 60 min, followed by the second heating stage at 180 °C for 240 min. The heating rate was set to 10 °C min⁻¹ for both heating stages. The specific surface area of the samples was calculated by applying the BET theory to the nitrogen adsorption data within the 0.06 – 0.30 P/P₀ range.

The polyHIPE skeletal densities (ρ P) (an average of 10 consecutive measurements) were evaluated using a fully automated, highly precision **helium pycnometry** (Micromeritics, model AccuPyc II 1340). To prevent the influence of moisture and impurities on the measurements, the polyHIPEs were thoroughly dried and purged with helium.

Cyclic voltammograms were taken on a potentiostat/galvanostat (Metrohm Autolab) at a scan rate of 100 mV/s at 25 °C in a three-electrode electrochemical cell. Electrolyte was 0.1 M

tetrabutylammonium hexafluorophosphate (TBAPF6) in acetonitrile. To prepare the working electrode, a volume of $10 \,\mu\text{L}$ of catalyst-ethanol suspension (12.5 mg of catalyst in 2.5 mL of absolute ethanol (Sigma Aldrich, Germany)) was dropped onto the surface of the screen-printed DropSens electrode. Reference electrode was a calomel electrode (HANNA instruments, model HI5412) and a counter electrode was made of platinum.

UV-Vis DR spectrophotometry was performed on a Perkin Elmer Lambda 35 UV-Vis spectrophotometer equipped with the accessory for powdered samples in order to record the UV-Vis diffuse reflectance spectra of the prepared materials. The background correction was performed with a white reflectance standard (range of 200 - 700 nm).

Photoluminescence (PL) emission spectra of the catalysts were recorded with a Perkin-Elmer UV-Vis fluorescence spectrometer using an excitation wavelength of 390 and 430 nm for the PAZ and PIMI samples, respectively. Prior to the examination, the catalyst samples were pressed in a holder to flatten the surface.

Preparation of 1,4-benzenedicarboxaldehyde dihydrazone

Hydrazine monohydrate (1 g, 20 mmol) was mixed with 10 mL ethanol and the resulting mixture was added dropwise to a solution of terephthalaldehyde (1.34 g, 10 mmol) in 10 mL ethanol. Thus obtained mixture was stirred for 2 h at room temperature. The yellow precipitate was collected and washed with 20 mL ethanol to obtain pure product. This compound has been reported previously.¹

m(product) = 1,195 g; yield: 74 %



 δH (400 MHz, CDCl₃, 25 °C, Me₄Si) 7.73 ppm (s, 2 H, Bz-H), 7.52 ppm (s, 4 H, Ph), 5.56 ppm (s, 4H, NH₂).

Preparation of PAZ and PAZi O/O polyHIPEs



PAZi:

N,N-dimethylformamide (DMF) (0.9 mL), terephthalaldehyde (402 mg, 3 mmol) and Pluronic F-127 (276 mg, 0.022 mmol) were added to the reaction vessel. The mixture was stirred for 3 min to ensure solubility. After reaching a transparent mixture, petroleum benzine (6 mL, b.p. 110-140 °C) was added dropwise under constant stirring to form a HIPE. To ensure uniformity of HIPE, the emulsion was mixed for another 5 min, followed by an addition of 155 μ L hydrazine monohydrate (150 mg; 3 mmol). The emulsion was further stirred for 1 min and afterward cured for 5 h at 60 °C. The material was purified via diffusion in 30 mL chloroform for 24 h and in 30 mL methanol solution (MeOH : H₂O = 1:1) for 24 h.

PAZ:

DMF (0.75 mL), 1,4-benzenedicarboxaldehyde dihydrazone (243 mg, 1.5 mmol) and Pluronic F-127 (250 mg, 0.020 mmol) were added to the reaction vessel. The mixture was stirred for 3 min to ensure solubility. After reaching a homogeneous yellow mixture, petroleum benzine (6 mL, b.p. 110-140 °C) was added dropwise under constant stirring to form a HIPE. To ensure uniformity of HIPE, the emulsion was mixed for another 5 min, followed by addition of terephthalaldehyde (201 mg; 1.5 mmol) in 0.25 mL DMF. The emulsion was further stirred for 2 min, and afterward cured for 5 h at 60 °C. The so formed polyHIPE was purified by diffusion using chloroform and isopropanol.

Preparation of PIMI O/O polyHIPE



Terephthalaldehyde (201 mg, 1.5 mmol) and Pluronic F-127 (190 mg, 0.015 mmol) were added into 0.5 mL DMF and the solution was stirred for 5 min to ensure homogeneous mixture. Afterward, 4.5 mL of petroleum benzene was added dropwise under constant stirring for HIPE formation. The 1,4-phenylenediamine was dissolved in DMF (0.25 mL) and added to the preformed terephthalaldehyde solution after stable HIPE was formed. The emulsion was further stirred for 30 s to ensure homogeneous incorporation of amine. Polymerization occurred already at room temperature, and was accelerated by heating to 50 °C for 5 h. The so formed polyHIPE was purified by diffusion using chloroform and isopropanol.

Preparation of PAZi polyHIPE beads through the O/O/O HIPE-based double emulsion

The stable O/O HIPE was prepared as described above (*in situ*) and filled into a syringe. The emulsion was then injected dropwise into the preheated sedimentation medium (silicon oil, 70 °C) using a needle (outer diameter 0.8 mm). After complete addition, the beaker with beads in sedimentation medium was put into the oven at 50 °C for 5 h.

FTIR spectroscopy



Figure S1. FTIR spectra of prepared polyHIPE materials.

The physical properties of PAZ- and PIMI-based polyHIPE

Table S1. Void and window sizes, densities and porosities of PAZ- and PIMI-based polyHIPEs.

Samples	PAZ	PAZi	PIMI
$d_{ m v}\pm\sigma$ [μ m] ^a	23.4±7	21.2±6.2	31.3±17
$d_{ m w}\pm\sigma$ [μ m] ^b	7.1±2	5.2±4.1	7.0±2
$ ho_{ m PH} [m g \cdot m cm^{-3}]^{c}$	0.127	0.115	0.0614
$ ho_{ m P} [m g \cdot m cm^{-3}]^{ m d}$	1.553	1.543	1.347
P [%] ^e	92	93	95
$SSA[m^2 \cdot g^{-1}]^f$	13	13	30

^aaverage void diameter; ^baverage window diameter; ^cdry polyHIPE density; ^dpolymer density determined by Hepycnometry, ^eporosities of monoliths, ^fspecific surface area

SEM characterization

The average void sizes were determined from SEM micrographs after scanning. Therefore, the mean and the standard deviations were drawn by manual measurements of diameters from a population of between 50-100 voids. Measured void values from SEM images were multiplied by a statistical factor of $2/3^{1/2}$ that allows a better estimation of the real cavity diameters.



Figure S2. SEM images of PAZi polyHIPE beads (A), PIMI (B) and PAZ (C) polyHIPE monoliths.

Cyclic voltammetry



Figure S3. Cyclic voltammograms of PIMI and PAZ polyHIPEs.

Thermogravimetric analysis (TGA)



Figure S4. Thermogravimetric curves (left) and the dTG curves (right) of prepared polyHIPEs.

The thermal stability of prepared materials was determined by TGA in the range of 0-700 °C under nitrogen atmosphere (20 mL/min) and a heating rate of 10 K/min. PAZ and PAZi show good thermal stability up to 300 °C, and PIMI even up to 370 °C.

Aniline degradation experiments

The degradation of aniline was measured by UV-VIS spectrophotometry. The maximum absorption of aniline is at $\lambda_{max} = 230$ nm, and this absorption was monitored during a 48-h degradation period. 100 mL of aqueous aniline solution (125 mg/L) with 100 mg of grinded PAZ polyHIPE as photocatalyst was stirred in the dark for 24 h to determine the amount of adsorbed aniline (13 wt%). The so prepared dispersion was irradiated on a SynLED parallel photoreactor ($\lambda_{max} = 465-470$ nm) under air, resulting in 67% degradation of aniline after 48 h. Control experiments with photocatalyst in the dark (7 days) and without photocatalysts but under light irradiation were carried out, showing no signs of aniline degradation. Additionally, we performed the photocatalytic degradation of aniline in the presence of isopropyl alcohol (20 mL) under argon atmosphere, as hydroxyl radical and ROS scavengers, respectively.

References

1 N. O. Mahmoodi, M. A. Zanjanchi, A. Aliakbar, T. Behzadi and F. Ghanbari, *Orient. J. Chem.*, 2011, **27**, 517–522.