Electronic Supplementary Material (ESI) for Chemical Communications

Inverse electron demand Diels-Alder (iEDDA) functionalisation of macroporous poly(dicyclopentadiene) foams

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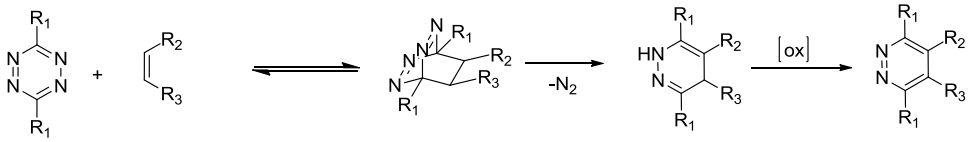


Fig. S1 iEDDA click chemistry (representative scheme)

Experimental

Instrumentation

NMR spectroscopy was performed on a Bruker Avanze 300 MHz spectrometer. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. The relaxation delay was set to 5 s for polymers in order to guarantee complete relaxation. Chemical shifts are given in ppm relative to a $SiMe_4$ standard. Solvent residual peaks ($CDCl_3$: 7.24 (^1H) and 77.23 ppm (^{13}C); dmso-d^6: 2.50 (^1H) and 39.51 (^{13}C), respectively) were used for referencing the NMR spectra. Peak shapes are indicated as follows: s (singlet), d (doublet), dd (doublet of doublet), dt (doublet of triplet), td (triplet of doublet), t (triplet), m (multiplet), b (broad), v (virtual splitting).

Gel permeation chromatography (GPC) was used to determine molecular weights and the polydispersity index (PDI) of the polymers. Measurements were carried out in THF with the following arrangement: a Merck Hitachi L6000 pump, separation columns of Polymer Standards Service (5 µm grade size) and a refractive-index detector from Wyatt Technology. For calibration, polystyrene standards purchased from Polymer Standard Service were used.

MALDI-TOF mass spectrometry was performed on a Micromass TofSpec 2E Time-of-Flight Mass Spectrometer. The instrument is equipped with a nitrogen laser (337 nm wavelength, operated at a frequency of 5 Hz) and a time lag focusing unit. Ions were generated by irradiation just above the threshold laser power. Positive ion spectra were recorded in reflectron mode applying an accelerating voltage of 20 kV and externally calibrated with a suitable mixture of poly(ethyleneglycol)s (PEG). The spectra of 100-150 shots were averaged. Analysis of data was done with MassLynx-Software V3.5 (Micromass/Waters, Manchester, UK). Samples were dissolved in THF (c=1 mg/mL), DCBT was used as matrix (c=10 mg/mL in THF). Solutions were mixed in the cap of a microtube in the ratio of 1 µL:10 µL. 0.5 µL of the resulting mixture were spotted onto the target and allowed to air dry.

Scanning electron microscopy images (SEM) and energy dispersive X-ray spectrums (EDX) were performed on a JWS-7515, JEOL Ltd. scanning electron microscope. Pieces of all samples were mounted on a carbon tab for better conductivity and afterwards a thin layer of gold was sputtered on samples surface prior to scanning analysis (for SEM investigations) or not sputtered for EDX investigations. SEM micrographs were taken at a magnification of 5000 X, at 7 mm working distance and 20 kV voltage applied while EDX experiments were performed at 15 mm working distance in the same apparatus under the same conditions.

True porosity (experimental porosity; Φ_{exp}) and the window size distribution of each sample were determined by mercury intrusion porosimetry (Micromeritic WIN9400 Series). The skeleton densities were obtained using helium pycnometry (AccuPyc 1330).

Materials

Unless otherwise noted, all reactions were carried out under argon in pre-dried glassware using Schlenk techniques. Materials were obtained from commercial sources (Aldrich, Fluka or Lancaster) and were used as received without further purification, if not stated otherwise. **M2** was obtained from Umicore, **G1** was obtained from Materia Inc. and **pyTz** was prepared according to a literature procedure.[1] CH_2Cl_2 was dried by distillation over CaH_2 and stored under an inert nitrogen atmosphere. Toluene was distilled prior to use.

Synthesis of reference pyridazines

3,6-Di(pyridin-2-yl)pyridazine[2]

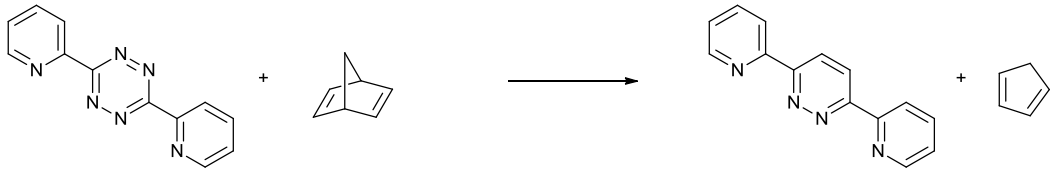


Fig. S2 Preparation of 3,6-dipyridin-2-yl)pyridazine

170 mg (0.720 mmol) of pyTz were dissolved in 5 mL of dichloromethane in a 20 mL scintillation vial. While stirring, 400 µL of norbornadiene (5.5 equiv., 3.93 mmol) were added which caused discoloration of the initially pink solution and the evolution of gas (nitrogen, cyclopentadiene). After 20 min, the reaction mixture was entirely discoloured. After stirring the reaction mixture overnight, excess norbornadiene and the solvent were evaporated and the resulting yellow solid was dried *in vacuo*.

^{1}H-NMR (δ, 20°C, 300 Hz, $CDCl_3$): ^{1}H: 8.73 (m, 4H, 6,6'', 3, 3''-H); 8.67 (s, 2H, 4',5'-H); 7.89 (ddd, 4, 4'' H); 7.39 (ddd, 5, 5''-H)

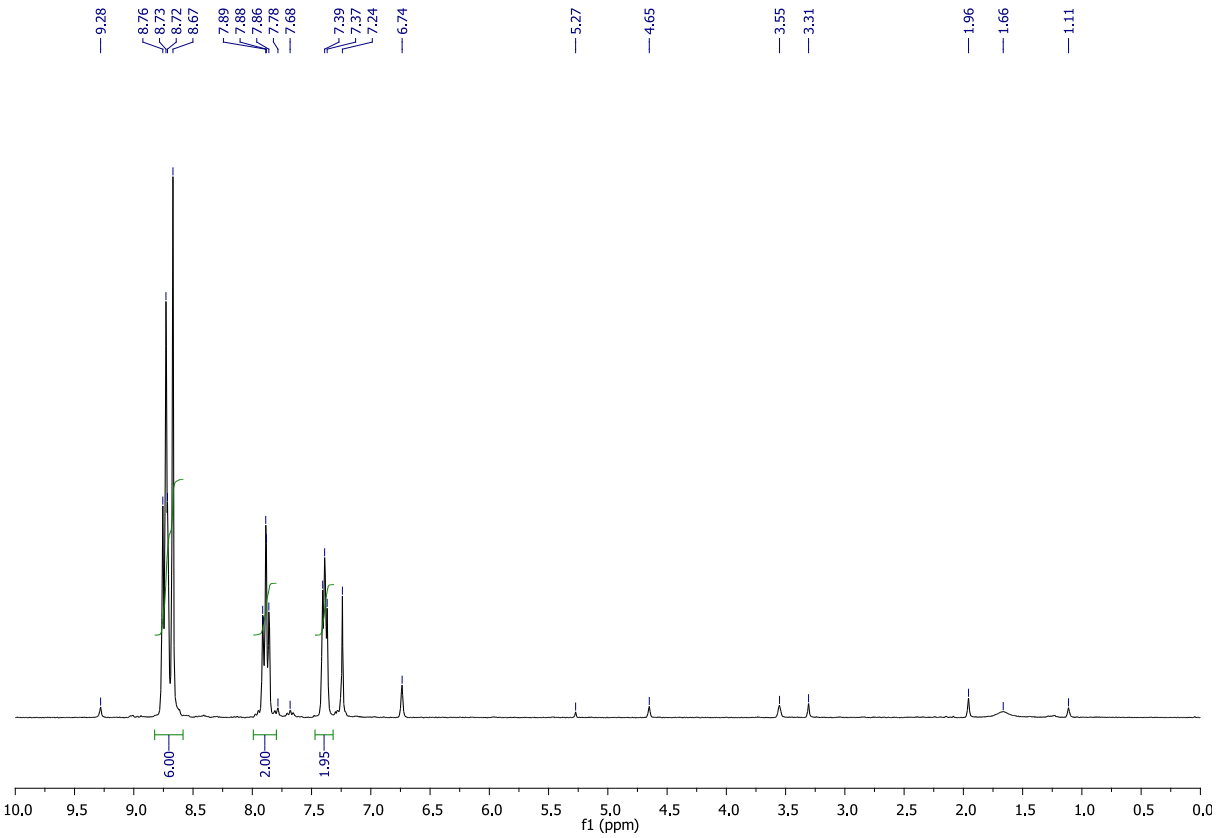


Fig. S3 ^{1}H NMR spectrum of 3,6-dipyridin-2-yl)pyridazine

(1,4-di(pyridin-2-yl)-6,7-dihydro-5H-cyclopenta[d]pyridazine)

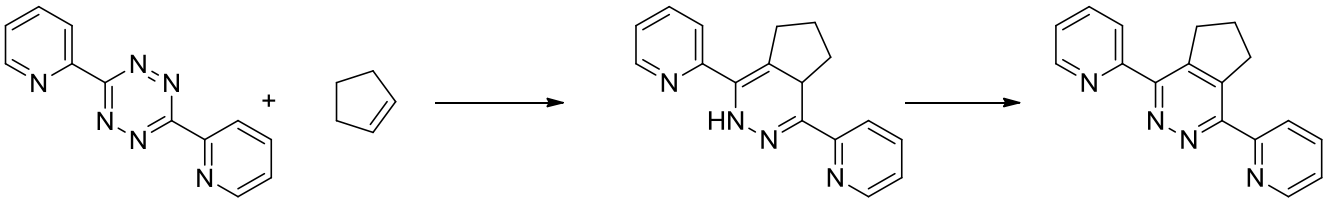
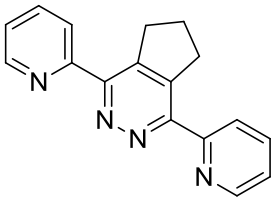


Fig. S4 Preparation of (1,4-di(pyridin-2-yl)-6,7-dihydro-5H-cyclopenta[d]pyridazine)

5 mg of pyTz were dissolved in 1.5 mL of dichloromethane in a 20 mL scintillation vial. 50 µL of cyclopentene (25 equiv.) were added while the reaction mixture was stirred. After 1 h, pyTz was already consumed as indicated by discolouration of the initially pink solution. Excess cyclopentene and the solvent were evaporated and the resulting yellow solid was dried *in vacuo*.



^{1}H-NMR (δ, 20°C, 300 Hz, $CDCl_3$): 8.72 (d, 2H, 6,6''-H); 8.57 (d, 2H, 3, 3''-H), 7.91 (td, 2H, 4, 4''-H), 7.36 (dd, 2H, 5, 5''-H), 3.53 (t, 4H), 2.15 (pentet, 2H)

The product was kept in the sealed NMR tube for one week and then, another ^{1}H NMR spectrum was recorded.

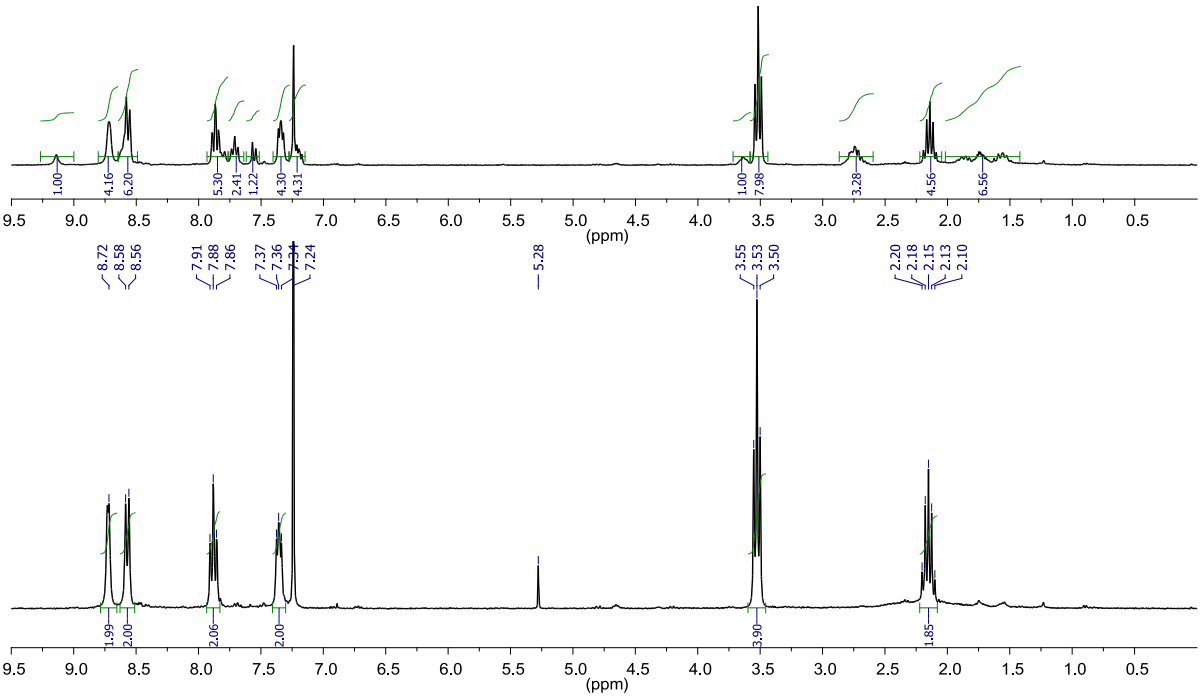


Fig. S5 ^{1}H NMR of 1,4-di(pyridin-2-yl)-4a,5,6,7-tetrahydro-2H-cyclopenta[d]pyridazine. Top: directly after product isolation, bottom: after 1 week (1,4-di(pyridin-2-yl)-6,7-dihydro-5H-cyclopenta[d]pyridazine is formed)

4-butyl-3,6-di(pyridin-2-yl)pyridazine

50 mg of pyTz (0.212.mmol) were dissolved in 2 mL of dichloromethane in a 20 mL scintillation vial. 265 µL of 1-hexene (2.12 mmol, 10 equiv.) were added and the reaction mixture was stirred. After 3 h, the reaction solution had turned from pink to yellow and thus, excess hexene and DCM were evaporated. The yellow solid residue was dried *in vacuo* and was purified using flash chromatography (silica, DCM:methanol 20:1). Yield: 37.5 mg.

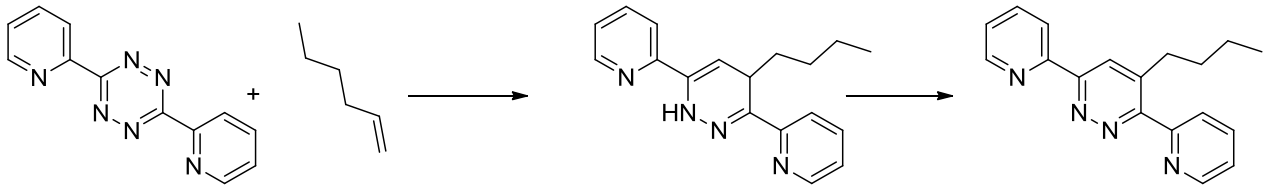
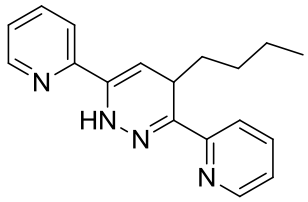


Fig. S6 Preparation of (1,4-di(pyridin-2-yl)-6,7-dihydro-5H-cyclopenta[d]pyridazine)

The product was kept in the sealed NMR tube for one week and then, another ^{1}H NMR spectrum was recorded.



^{1}H-NMR (δ, 20°C, 300 Hz, $CDCl_3$): 9.22 (bs, 1H, NH), 8.55 (t, 2H), 8.9 (dt, 2H), 7.67 (mult., 3H), 7.22-7.16 (2t, 2H), 5.62 (dd, 1H), 4.29 (m, 1H), 1.5 (m, 2H), 1.3-1-2 (2m, 4H), 0.75 (t, 3H)

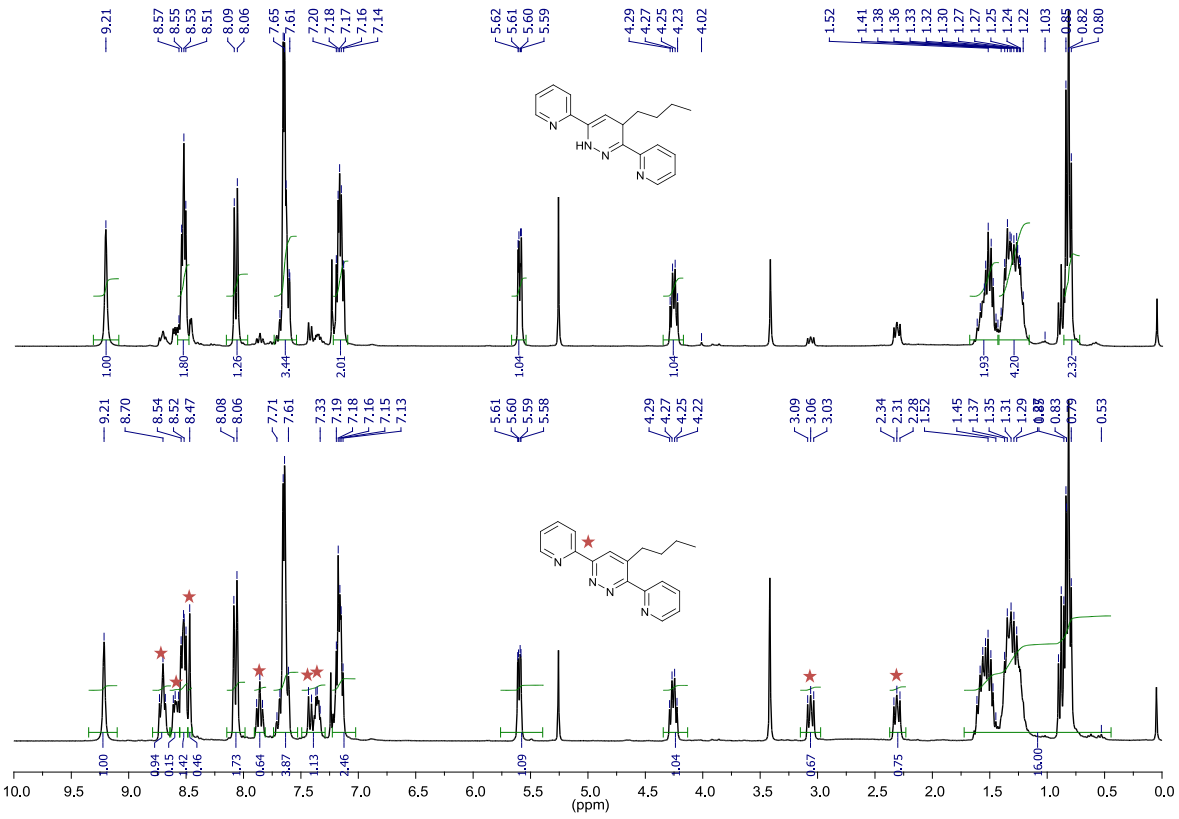


Fig. S7 ^{1}H NMR of 5-butyl-3,6-di(pyridin-2-yl)-1,4-dihydropyridazine. top: directly after product isolation, bottom: after 1 week (approx. 40% conversion), red stars mark peaks assigned to the pyridazine product

Preparation of oligo-DCPD

500 mg of DCPD (Aldrich, 3,78 mmol, 100 equiv.) were placed into a Schlenk tube and dissolved in 50 mL of dry, degassed dichloromethane. The solution was cooled to 0°C. Then, 31.10 mg (1 equiv.) of **G1** (bis(tricyclohexylphosphine)benzylidine ruthenium(IV) dichloride) were added at once. The colour change from dark purple to red indicating initiation was significantly slower than at room temperature. After 5 min, the solution became turbid and polymerization was continued until about 75% conversion was achieved (approx. 9 min, estimated by TLC, cyclohexane/ethyl acetate 9:1). Then, 500 µL of ethyl vinyl ether were added to terminate the reaction while it was allowed to warm up to room temperature. After 30 minutes, the reaction mixture was evaporated to dryness. Then, 3 mL of toluene were added to the residue and the suspension was left to stand overnight. The supernatant was removed and precipitated into 200 mL of chilled methanol (-20°C). The formed precipitate was separated off by centrifugation and dried *in vacuo*.

GPC: Mn=1.67 kDa, PDI=2.41

IR 3045, 2925, 2849, 1448, 1356, 1309, 972, 939, 908, 800, 732, 709, 575 cm^{-1}

^{1}H NMR (see Fig. 3 in the main article): 5.60 (bs), 5.43 (bs), 5.37 (bs), 5.31 (bs), 3.15 (bs), 2.73 (bs), 2.53 (bs), 2.18 (bs), 1.48 (bs), 1.20 (d), 1.16 (d)

Modification of oligo-DCPD

6.56 mg of oligo-DCPD (0.0496 mmol) were placed in an NMR tube together with 5.86 mg of pyTz (0.5 equiv. per repeating unit, 0.0248 mmol) and dissolved in 750 µL of $CDCl_3$. The resulting solution was then measured 1 h after addition and left to stand for further 24 h at room temperature. After this time, another ^{1}H NMR spectrum was recorded. Then, FT-IR spectra (Fig. S8) were recorded of both the converted sample and a control experiment (no tetrazine added).

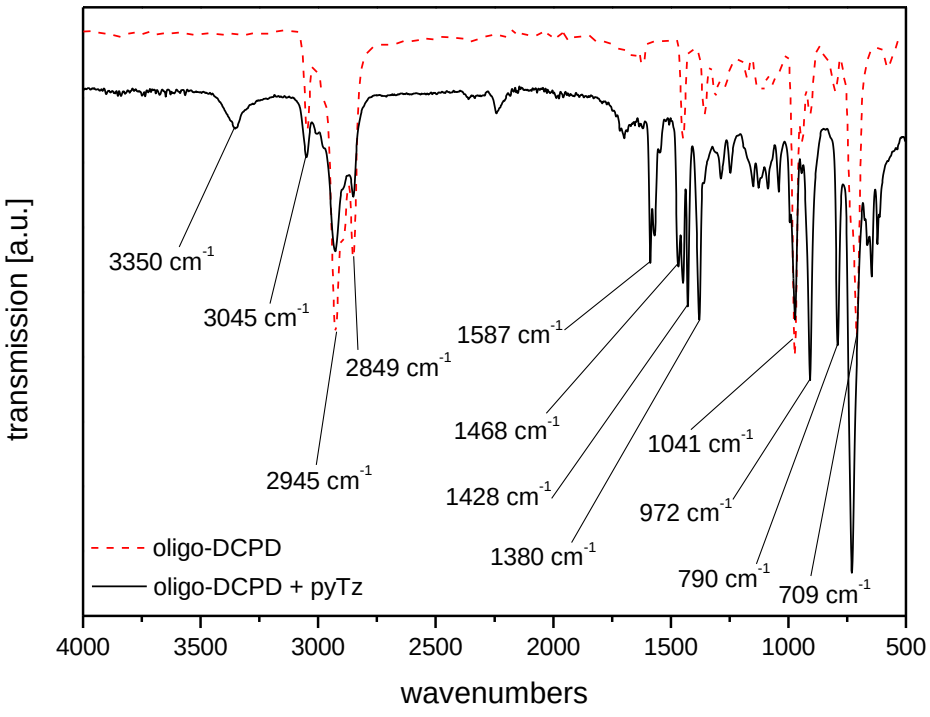


Fig. S8 FT-IR spectra of oligo-DCPD. a) stored under vacuum for 1 week b) after addition of 0.5 equiv pyTz, 24 h

Preparation of polyHIPE monoliths

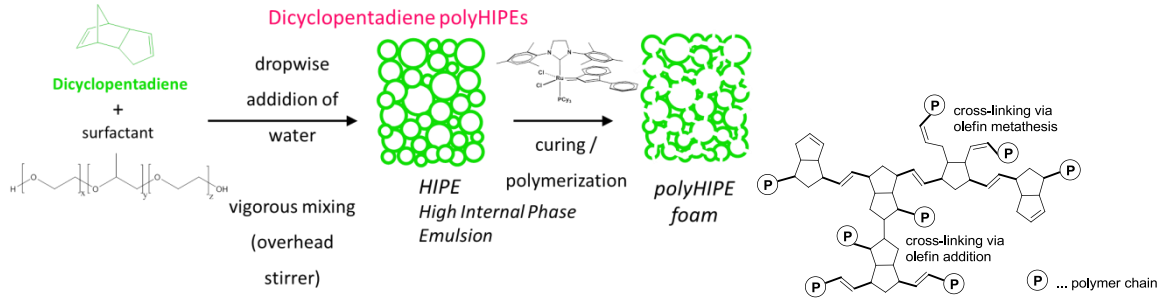


Fig. S9 Preparation of DCPD poly-HIPEs

Dicyclopentadiene (Fluka, 4.4 g, 33 mmol) and Pluronic L121 (Sigma-Aldrich, 0.5 g) were placed in a reactor and the mixture was stirred with an overhead stirrer at 400 rpm. 18 mL of deionised water was added drop wise under constant stirring. Upon further stirring for 1 h a uniform emulsion formed and M2 (Umicore, 0.015 mol % (with respect to DCPD) dissolved in 1 cm^3 of toluene) was added. The formulation was transferred to a mould and cured (80°C) for 2 h. The pDCPD monoliths were purified by using Soxleth extractions in THF, dichloromethane and acetone (24 h each) and dried *in vacuo*.

Labeling experiments

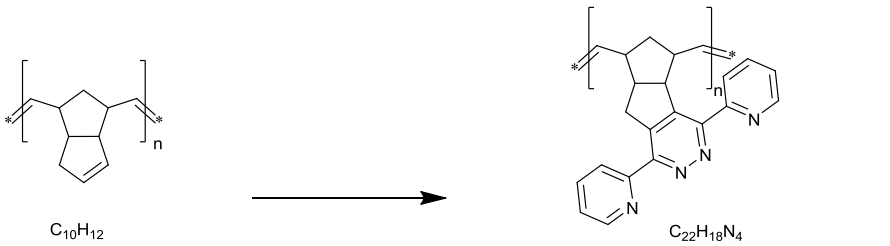


Fig S10 Labeling of pDCPD with pyTz

The purified pDCPD foams were placed in scintillation vials containing THF or methanol (4 mL) and 0.5 or 0.1 equiv of pyTz (with respect to DCPD as a repeating unit, Table S1/Fig. S10), respectively. The labeling experiment using 0.1 equiv. of pyTz was finished within 48 h. Due to limited solubility of pyTz in THF, when 0.5 equiv were used, the scintillation vial was put into a drying oven (60°C) after 24 h. After another 14 h, also the sample containing 0.5 equiv. of pyTz was discoloured. Therefore, the experiment using 0.1 equiv. of pyTz was repeated at 60°C and the labelling process was finished within 3h. When methanol was used as solvent, neither the 0.1 nor the 0.5 equivalents were discoloured, even after 9d, therefore the reactions were stopped and the monoliths were purified using the same procedure as for the samples immersed in THF.

Table S1 Used amounts for labelling experiments.

	Mass [mg]	**n [mmol]**	**equiv.***
polyDCPD monolith	200.0 mg	1.513 mmol*	1.0
py Tz	35.7 mg	0.151 mmol	0.1
	178.7 mg	0.756 mmol	0.5

*with respect to DCPD repeating units $(C_{10}H_{12})_n$

The resulting monoliths which are coloured yellow because of the grafted pyridazines were rinsed with acetone and stored in acetone for 24 h, then, the supernatant was discarded. This process was repeated and after drying *in vacuo*, the monoliths were subjected to elemental analysis.

Elemental analysis

Elemental analysis was performed on an Elementar Vario EL III 2 weeks after sample preparation and 2 months after sample preparation (see Table S2). Results presented are average values of two independent measurements (error bars in Fig. 2 represent the according standard deviation).
Corrected values are calculated under the assumption that neither pDCPD nor pyTz should contain any oxygen, for example:

$$\%C_{corr} = \frac{\%C}{\%C + \%H + \%N} \qquad \text{(S1)}$$

Table S2 Elemental analysis (mean values are given) of iEDDA modified DCPD polyHIPEs

treatment	unmodified [a]	0.1 equiv pyTz, THF, RT [b]	0.1 equiv pyTz, THF, 60°C [a]	0.5 equiv pyTz, THF [c]	0.1 equiv pyTz MeOH [b]	0.5 equiv pyTz, MeOH [b]
empirical formula	$(C_{10}H_{12})_n$	$(C_{10}H_{12})_{0.9}\cdot(C_{22}H_{18}N_4)_{0.1}$	$(C_{10}H_{12})_{0.9}\cdot(C_{22}H_{18}N_4)_{0.1}$	$(C_{10}H_{12})\cdot(C_{22}H_{18}N_4)$	$(C_{10}H_{12})_{0.9}\cdot(C_{22}H_{18}N_4)_{0.1}$	$(C_{10}H_{12})\cdot(C_{22}H_{18}N_4)$
CHN, calc'd	C: 90.85; H 9.15	C: 88.02; H 8.31; N 3.67		C: 81.67; H 6.43; N 11.90	C: 88.02; H 8.31; N 3.67	C: 81.67; H 6.43; N 11.90
CHN, Found	C: 77.69; H: 7.90; O: 14.41	C: 67.43; H: 6.52; N: 3.09; O: 22.95	C: 73.58; H: 7.06; N: 3.33; O: 16.04	C: 74.22 H: 5.99 N: 11.47 O: 8.32	C: 62.81; H: 6.36; N: 1.02; O: 29.81	C:63.74; H: 6.37; N: 1.50; O: 28.39
CHN, corrected [d]	C: 90.78; H: 9.22	C: 87.52; H: 8.46; N: 4.01	C: 87.63; H: 8.41; N: 3.96	C: 80.95 H: 6.54 N: 12.51	C: 89.49; H: 9.06; N: 1.45	C: 89.01; H: 8.89; N: 2.10
Theoretical grafting yield (total amount of double bonds)		5%		25%	5%	25%
Theoretical grafting yield (per repeating unit)		10%		50%	10%	50%
Mass% (pDCPD)	100	76	76	24	91	87
Mass% ($pyTz_{grafted}$)		24	24	76	9	13
Pyridazine content [mmol/g]		0.72	0.71	2.23	0.66	0.72
Mole% (pDCPD)	100	89	89	45	96	95
Mole% ($pyTz_{grafted}$)		11	11	55	4	5
Observed grafting degree (total amount of double bonds) [%]		5.5%	5.5%	27%	2%	2.5%
Observed grafting degree (per repeating unit) [%]		11%	11%	55%	4%	5%
	% of theory	**109%**	**111%**	**110%**	**36%**	**11%**

[a] measured 2 weeks after sample preparation, [b] measured 2 months after sample preparation, [c] average of two pieces of the same monolith, [d] oxygen omitted (according to Eq. S1)

We assumed (in accordance with the ^{1}H NMR and FT-IR results) that all dihydropyridazine groups in the modified monoliths are present in their oxidised form and that the nitrogen content in modified monoliths can be attributed solely to grafted pyridazines (as shown in Fig. S10).

Thus, the amount of grafted pyridazines in mmol/g as well as in mol% was calculated from the nitrogen content of the samples:

$$mass\%[\,pyTz_{grafted}] = \frac{\%N}{16.56}\cdot 100 \qquad \text{(S2)}$$

$$n[pyTz_{grafted}] = \frac{\frac{\%N}{16.56}}{338.41} \cdot 1000 \text{ [mmol/g]} \quad \text{(S3)}$$

$$n[DCPD] = \frac{\left(1 - \frac{\%N}{16.56}\right)}{132.20} \cdot 1000 \text{ [mmol/g]} \quad \text{(S4)}$$

$$mole\%[pyTz_{grafted}] = \frac{n[pyTz_{grafted}]}{n[pyTz_{grafted}] + n[DCPD]} \cdot 100 \quad \text{(S5)}$$

Impregnation with Eu^{3+}

A small piece of monolith (100 mg) modified with 0.5 equiv of pyTz in THF (approx. 2.2 mmol pyridazines/g, 0.22 mmol) was immersed in a solution (100 mg ($Eu(NO_3)_3 \cdot 5\ H_2O$), 0,233 mmol, in 2 mL of acetonitrile) of europium nitrate trihydrate and the reaction was monitored visually with the help of a mercury lamp (λ=365 nm). Already after 10 min, bright red phosphorescence (which is typical for Eu(III) coordination compounds) was observed. After 6h, excess solvent was removed and the monolith was dried *in vacuo*.

SEM characterisation of the monoliths

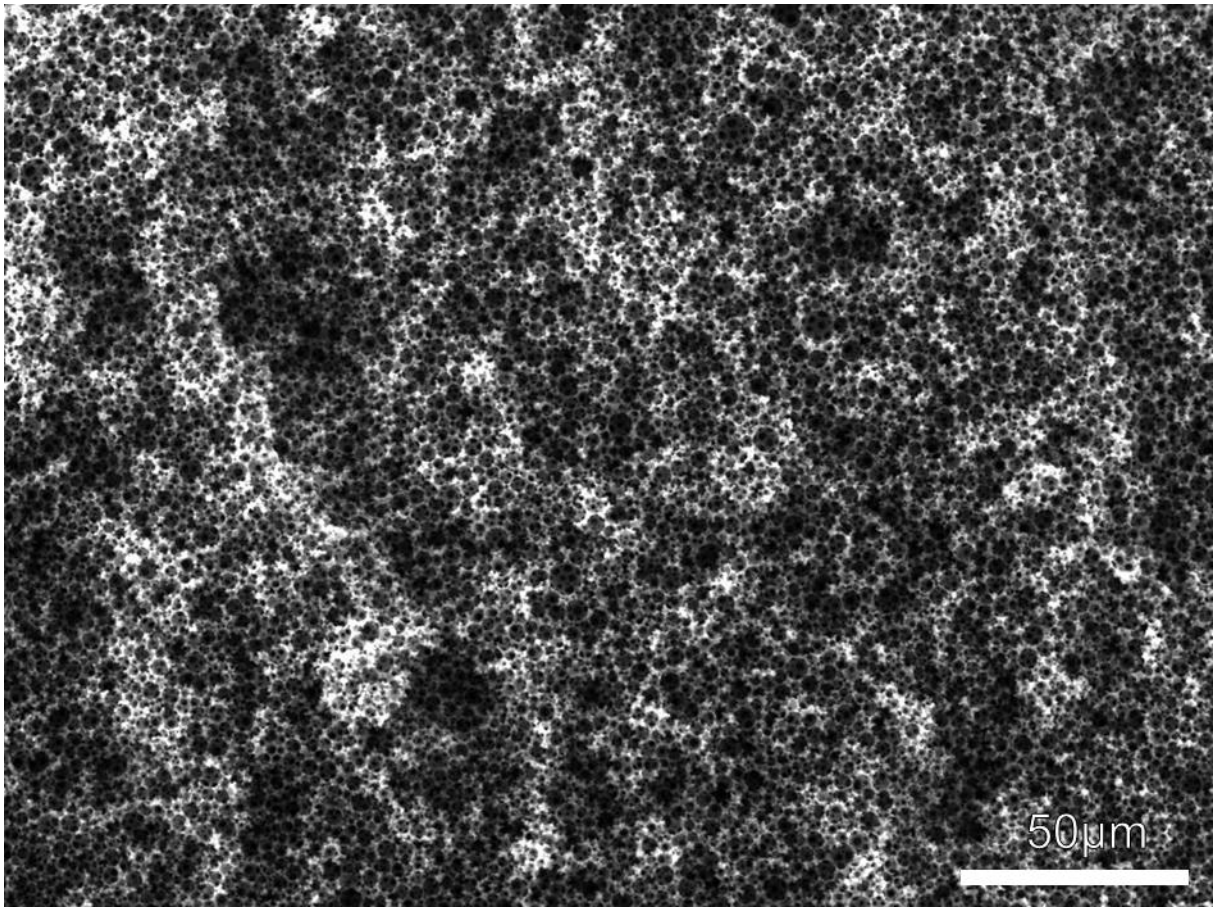


Fig. S11 SEM image of unmodified pDCPD foam (5000x)

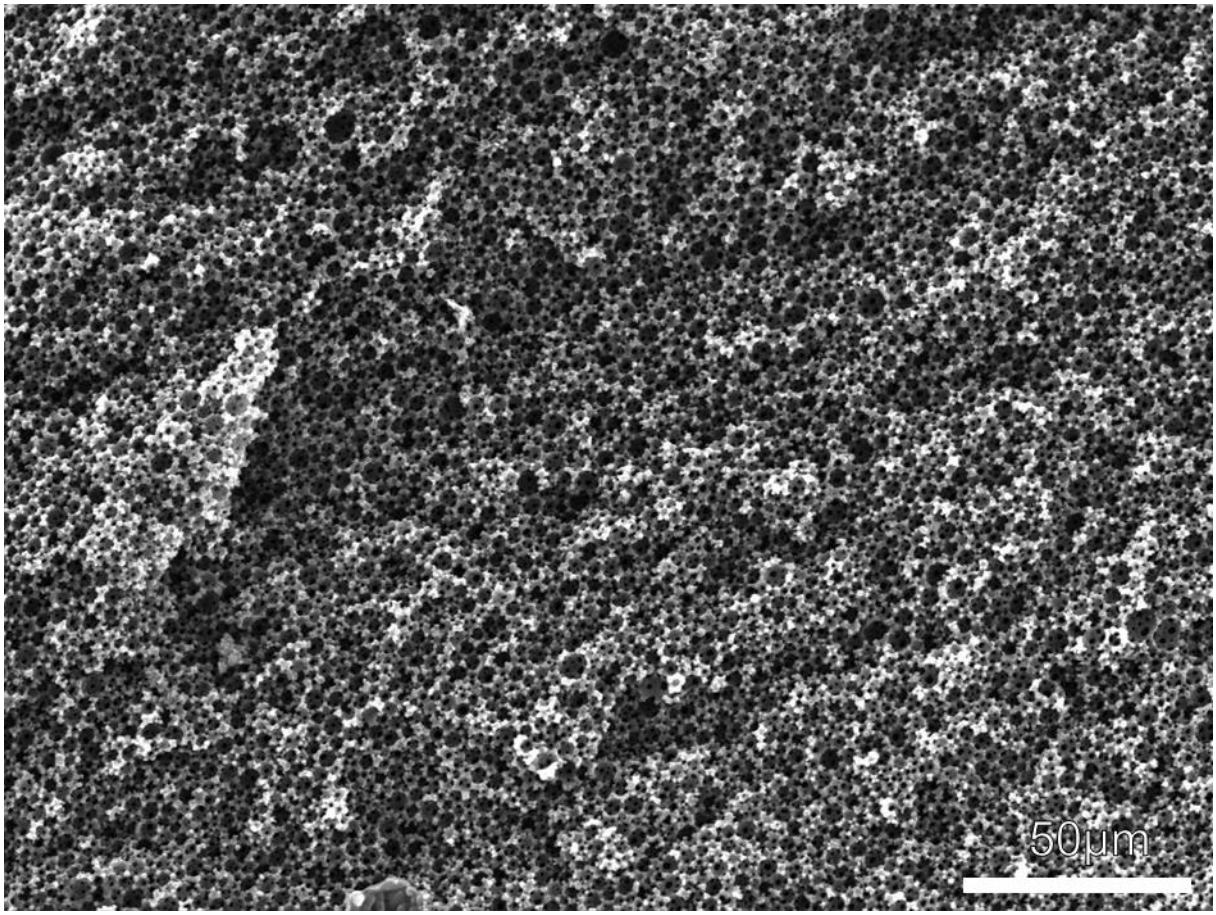


Fig. S12 SEM image of tetrazine labelled pDCPD (0.5 equiv. pyTz in THF) foam (5000x)

Porosity

Table S3 Porosimetry results

	unmodified [3]	0.5 equiv pyTz, THF	0.1 equiv pyTz, MeOH
porosity Φ_{theor} [a]	80	80	80
porosity Φ_{exp} [b]	80±1%	85±1%	70±1%
Skeletal density [g cm^{-3}] [c]	1.20	1.75	1.52
Av. Window diameter [µm] [b]	1.1	0.6	0.5

[a] according to emulsion formulation; [b] Experimental porosity and average window diameter assessed from mercury porosimetry data; [c] determined by helium pycnometry

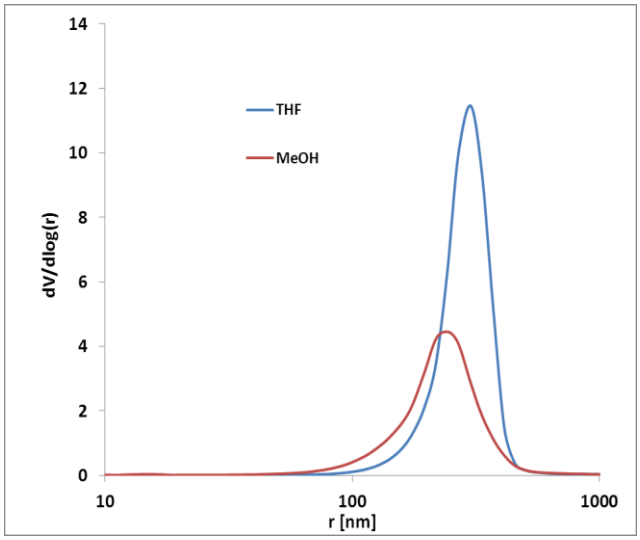
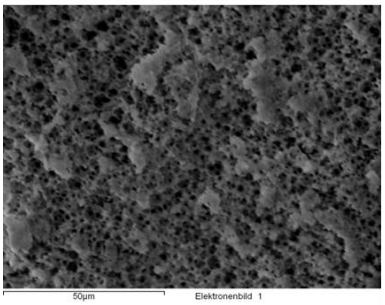
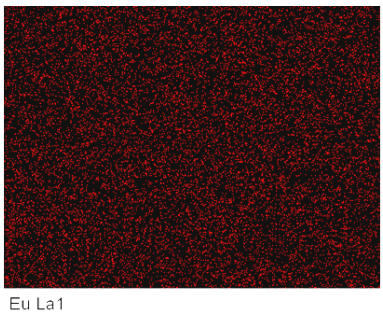


Fig. S13 Pore size distribution plot from mercury porosimetry data

EDX analysis

Table S4 SEM image, EDX image and elemental analysis

SEM image (scale bar= 50µm)	Eu distribution (scale bar= 50µm)	element	mass%	at%
		C K	76.71	83.55
		O K	19.64	16.06
		Si K	0.20	0.10
		Eu L	3.45	0.30

Preparation of bis(3,6-di(pyridin-2-yl)pyridazine)europium(III)nitrate[4]

50 mg of 3,6-di(pyridin-2-yl)pyridazine (0.213 mmol) were suspended in dry acetonitrile (2 mL) in a 20 mL scintillation vial. Then, 91.36 mg (1 equiv., 0.213 mmol) of europium(III)nitrate pentahydrate were dissolved in 2 mL of dry acetonitrile and added dropwise. Upon addition, the reaction mixture turned deep yellow and red europium emission was observed when the solution was viewed under UV light (365 nm). The reaction mixture was stirred for two days and the formed white precipitate was collected by filtration. Yield 86 mg (99%).

MALDI-TOF-MS $[Lig_2Eu(NO_3)_2]^+$ calcd. 743.0766, found 743.0757

[1] H. Bakkali, C. Marie, A. Ly, C. Thobie-Gautier, J. Graton, M. Pipelier, S. Sengmany, E. Léonel, J.-Y. Nédélec, M. Evain and D. Dubreuil, *Eur. J. Org. Chem.*, 2008, 2156.
[2] R. N. Warrener and P. A. Harrison, *Molecules*, 2001, **6**, 353.
[3] S. Kovačič, N. B. Matsko, K. Jerabek, P. Krajnc and C. Slugovc, *J. Mater. Chem. A.*, 2013, **1**, 487.
[4] G. Katsagounos, E. Stathatos, N. B. Arabatzis, A. D. Keramidas and P. Lianos, *J. Lumin.*, 2011, **131**, 1776.