Aromatic Polymers made by Reductive Polydehalogenation of Oligocyclic Monomers as Conjugated Polymers of Intrinsic Microporosity (c-PIMs)

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Introduction

Poly(indenofluorene) **P55** and poly(diindenonaphthalene) **PDIN**; are low bandgap polyhydrocarbons with long wavelength absorption features ranging into the near infrared (NIR) region.[1,2] The low bandgap character was assigned to the contribution of quinoidal resonance states to the electronic ground state mainly driven by the twisted exocyclic double bonds as result of the crowded steric situation around these double bonds. In continuation of this work, we have now tested related pentacyclic tetrachloro-monomers that contain 7-membered (cycloheptatriene) instead of the initially used 5-membered (cyclopentadiene) connector rings by introducing one (**M57**)[3] or two additional vinylene groups (**M77**)[4] into the monomers in a reductive polyolefination protocol developed by our group to yield the new polymers **P57**, **P77** and **P55/77**.

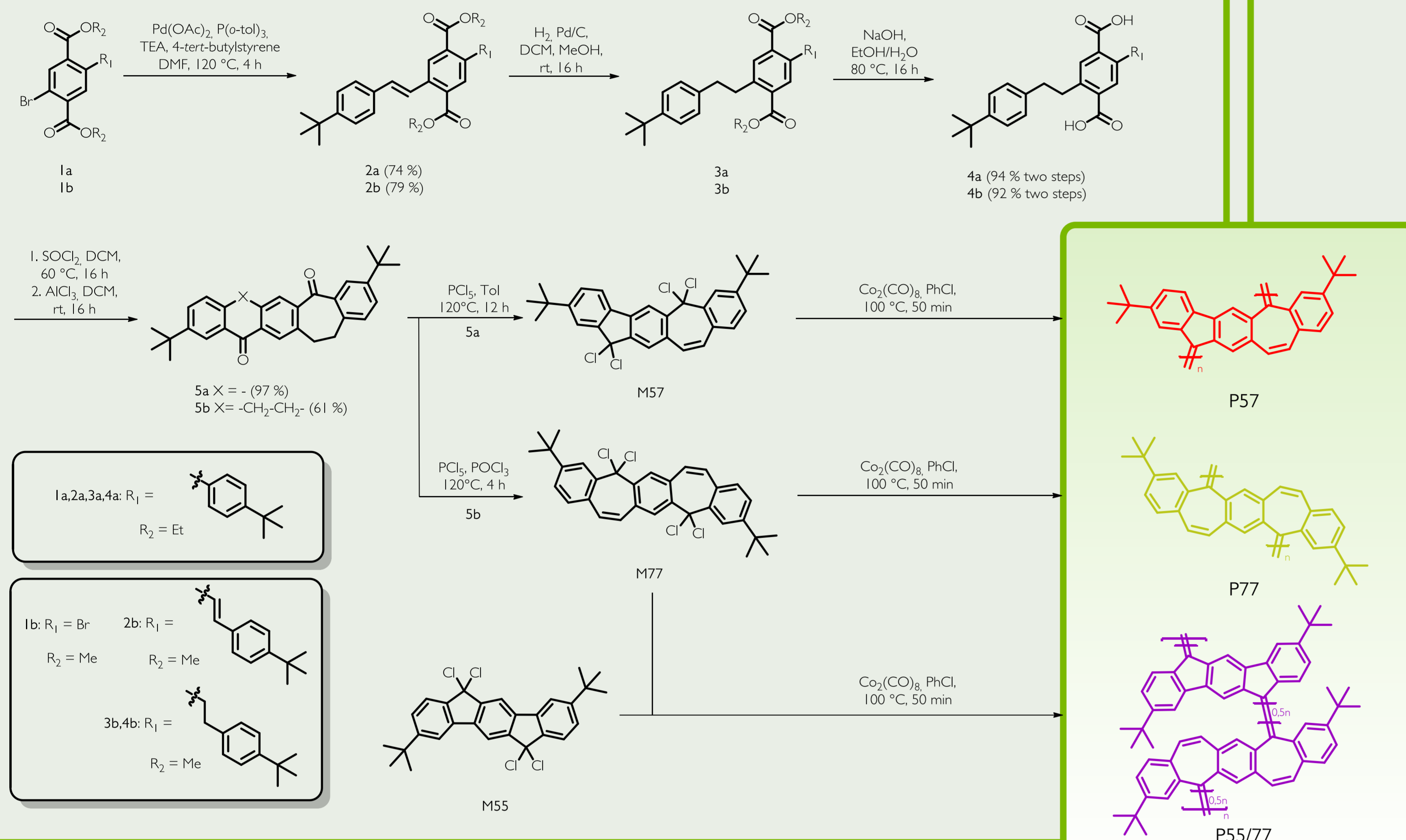### Synthetic pathway for novel polymers P57, P77 and P55/77

Figure 1 Synthetic pathway for polymers P57, P77 and P55/77.

Absorption properties for polymers containing bistricyclic aromatic ene (BAE) motifs

- „folded"
- effective conjugation barrier -
  no quinoidal contributions to
  ground state

- „twisted"
- conjugation allowed
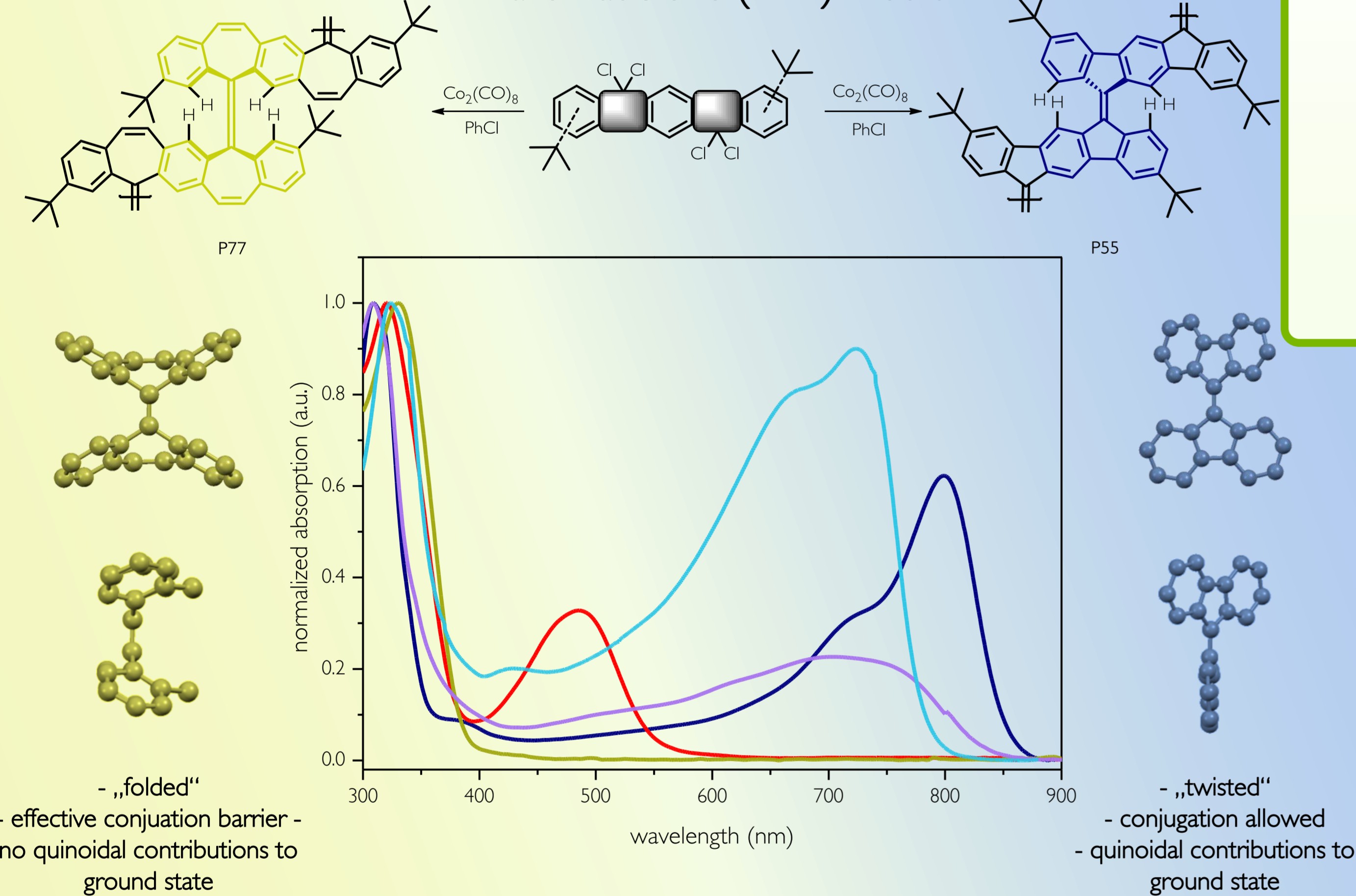- quinoidal contributions to
  ground state

Figure 2 left and right: Structural distortion for reduction of steric strain in the fjord area of polymers P55 and P77[5,6]; center: Normalized absorbtion spectra for polymers P57, P77, P55/77, P55 (PIF) and P55/77 in CHCl₃.
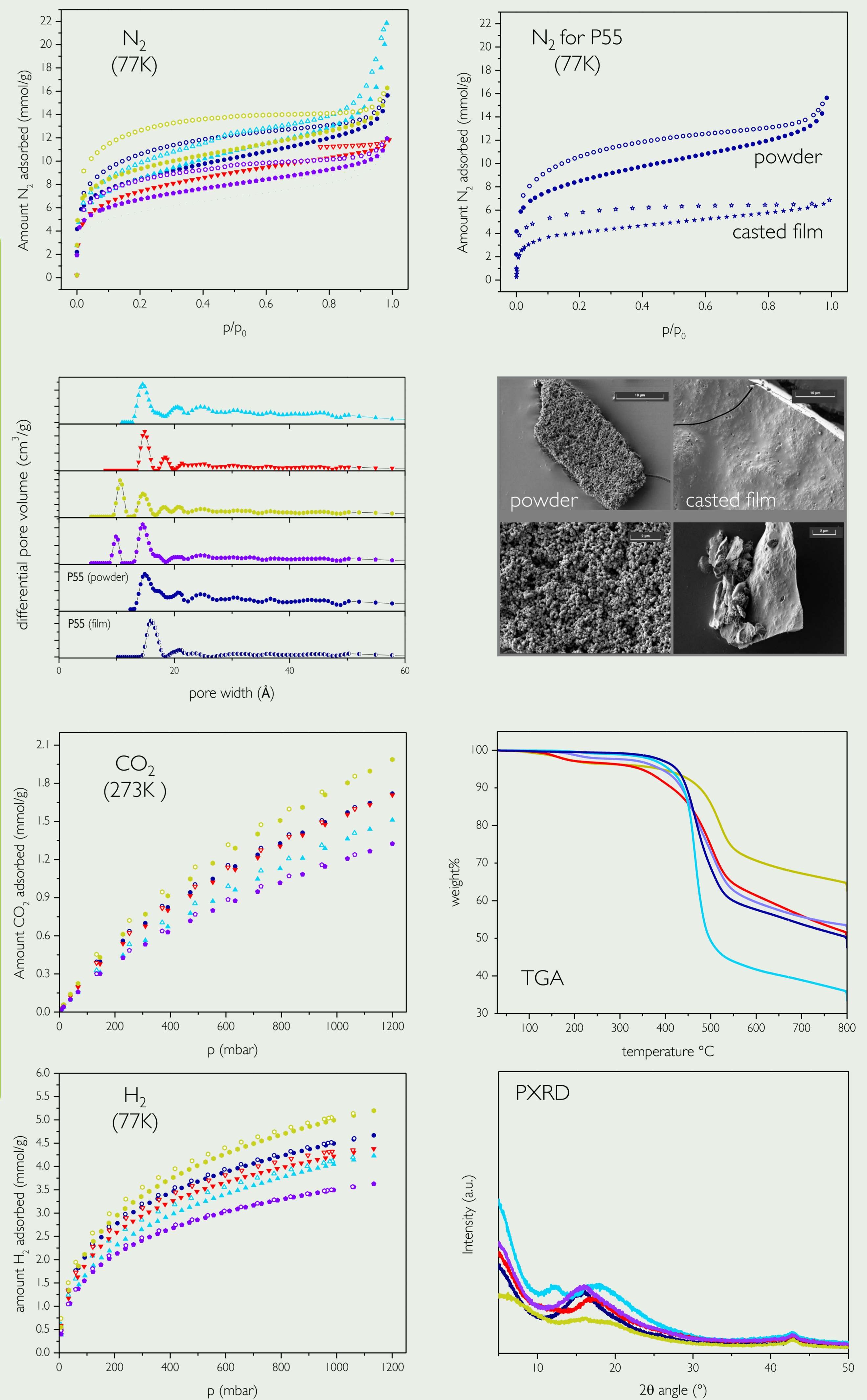
Polymer	M_n (kDa)	M_w (kDa)	M_w/M_n	DP	λ_{max} (nm)	S_{BET} (m²/g)	V_{total} (cm³/g)	V_{micro} (cm³/g)	H₂ uptake (77 K)[a] [mmol/g]	CO₂ uptake (273 K)[a] [mmol/g]
P57	10.4	14.4	1.4	26	485, 321	609	0.39	0.17	4.3	1.6
P77	13.2	20.7	1.6	32	331	757	0.58	0.22	5.1	1.8
P55/77	5.5	7.4	1.4	14	705, 309	543	0.41	0.15	3.6	1.2
P55	17.0	40.0	2.4	47	799, 309	687[b] (333[c])	0.51	0.18	4.6	1.6
PDIN	25.0	57.0	2.3	61	724, 324	691[d]	0.68	0.16	4.1	1.4

Table 1 Molecular weights, degree of polymerization, optical properties and BET surface areas for polymers P57, P77, P55/77, P55 and PDIN; [a] Uptake was determined at 1 bar. [b] Powder sample with a M_n: 7.2 kDa; M_w: 13.9 kDa. [c] after drop-casting the sample from chloroform solution. [d] Powder sample with a M_n: 5.3 kDa; M_w: 11.0 kDa.

Figure 3 Nitrogen (77K), carbon dioxide (273K) and hydrogen (77K) adsorption (filled symbols) and desorption (open symbols) isotherms, pore size distributions, TGA, PXRD and SEM data for polymers P57 (red), P77 (yellow), P55/77 (purple), P55 (deep blue) and PDIN (light blue).

Conclusion and outlook

- Three novel polymers **P57**, **P77** and **P55/77** have been generated from pentacyclic bisgeminal tetrachlorides by reductive dehalogenation polycondensation with dicobalt octacarbonyl.

- Interrupted conjugation along the tetrabenzoheptafulvalene building blocks (Figure 2, yellow) allows tuning of the absorption properties of the aromatic polymers.

- **P77** shows highest BET surface area in the polymer series with one of the highest values measured for soluble c-PIMs until know.

- In contrast to microporous c-PIMs bearing spiro moieties, tetrabenzopentafulvalene based c-PIMs show a pronounced electronic conjugation along the polymer backbone with the exocyclic double bonds as efficient kinks within the polymer backbone.

Acknowledgements

[1] H. Reisch, U. Wiesler, U. Scherf, N. Tuytuylkov, *Macromolecules* **1996**, 29, 8204. [2] E. Preis, U. Scherf, *Macromol. Rapid Commun.* **2006**, 27, 1105. [3] X. Yang, X. Shi, N. Aratani, T. P. Goncalves, K.-W. Huang, H. Yamada, C. Chi, Q. Miao, *Chem. Sci.* **2016**, 7, 6176. [4] I. Agranat, D. Avnir, *J. Chem. Soc. Perkin Trans.* **1974**, 1155. [5] K. S. Dichmann, S. C. Nyburg, F. H. Pickard, J. A. Potworowski, *Acta Cryst. B* **1974**, 30, 27. [6] J. S. Lee, S. C. Nyburg, *Acta Cryst. C* **1985**.