Supplementary Information

Chemical vapour deposition of metalloporphyrins: A simple route towards the preparation of gas separation membranes

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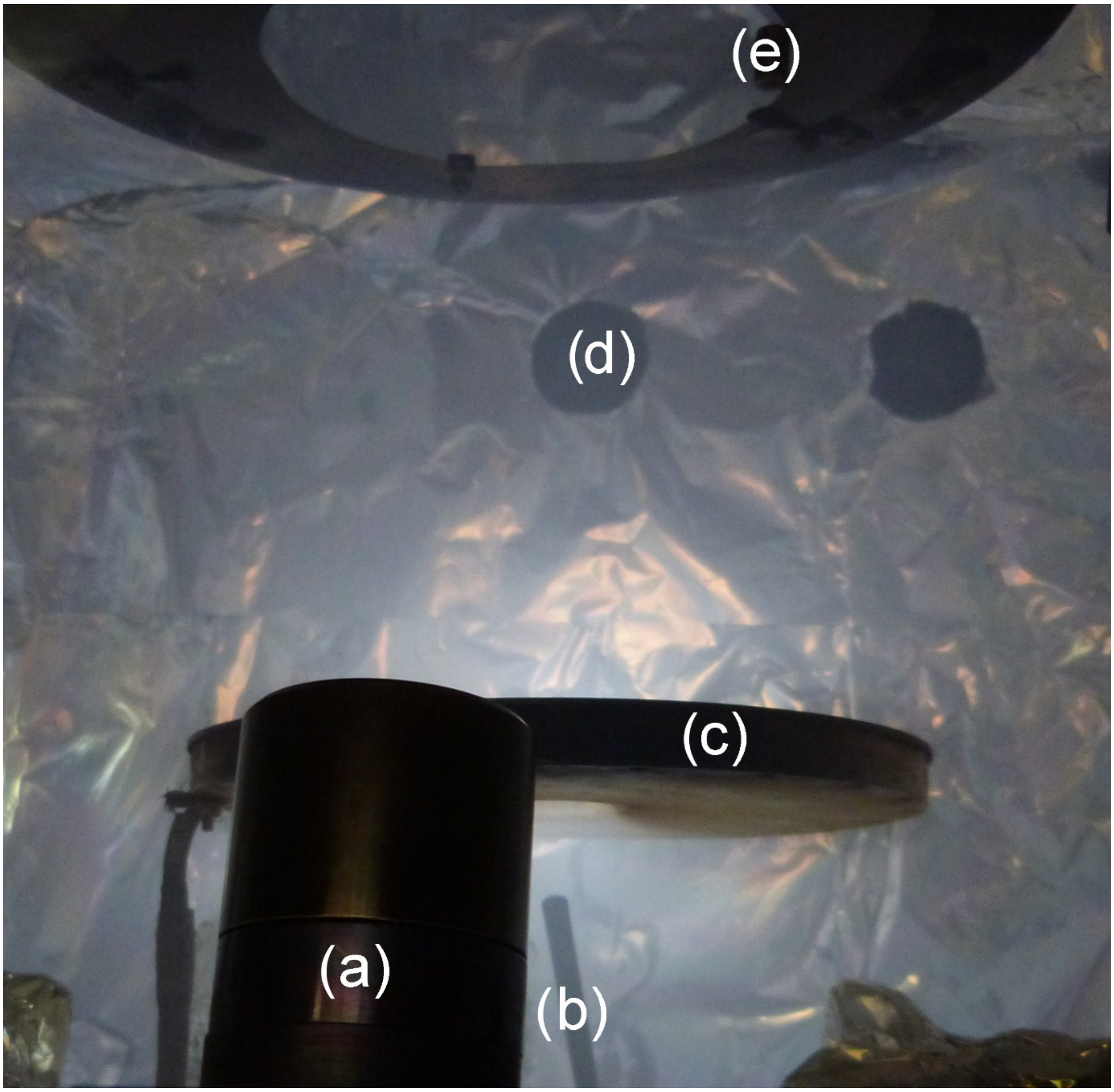

Figure S1. Photograph of the iPECVD reactor in operation. (a) The metalloporphyrin building units, *i.e.* ZnTPP, are evaporated from a crucible resistively heated at 275°C and located on the vicinity of the RF discharge below the substrate holder. (b) The initiator, *i.e.* TBPO, flows across (c) a circular high voltage RF electrode which sits below (e) the substrate holder on which the coating is formed. (d) The co-monomer, *e.g.* styrene or DVB, is introduced via a needle valve.

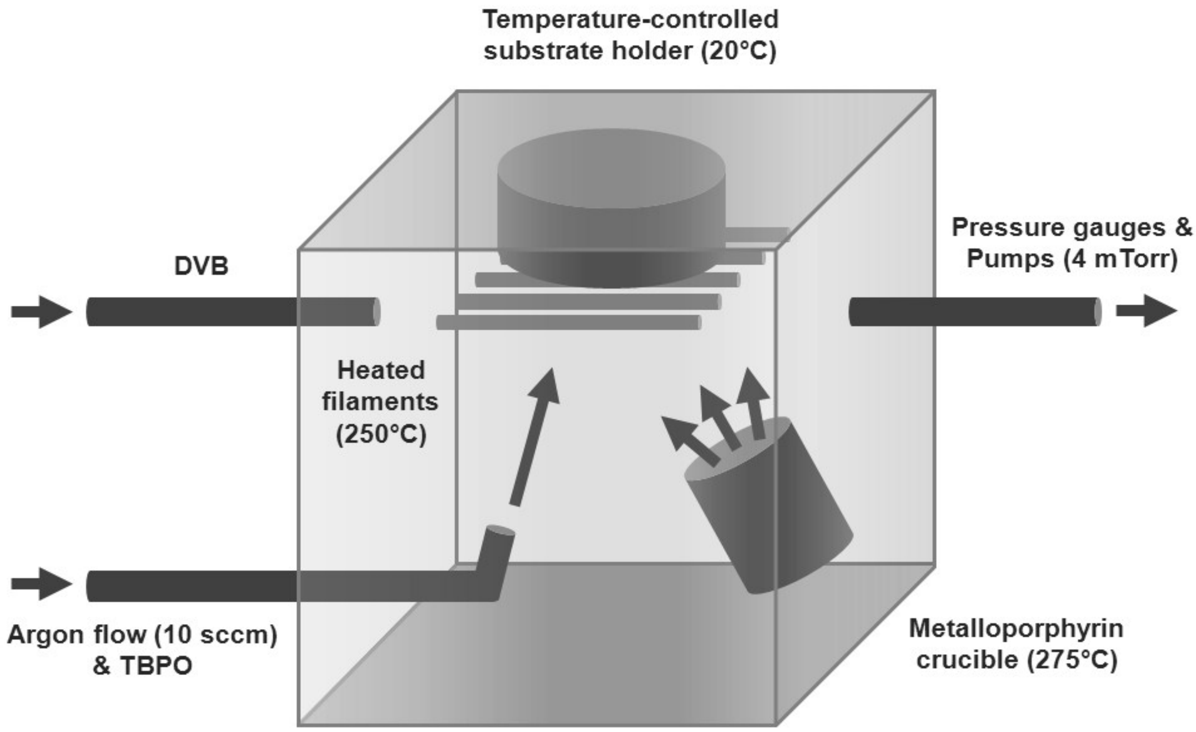

Figure S2. Schematic representation of the iCVD reactor setup. The initiator, *i.e.* TBPO, the metalloporphyrin building units, *i.e.* ZnTPP, and the co-monomer, *i.e.* DVB, are injected into the vacuum chamber where they meet resistively heated filaments (250°C). The initiator breaks down into radicals, potentially starting the free-radical polymerization of the metalloporphyrin building units at the substrate surface (20°C).

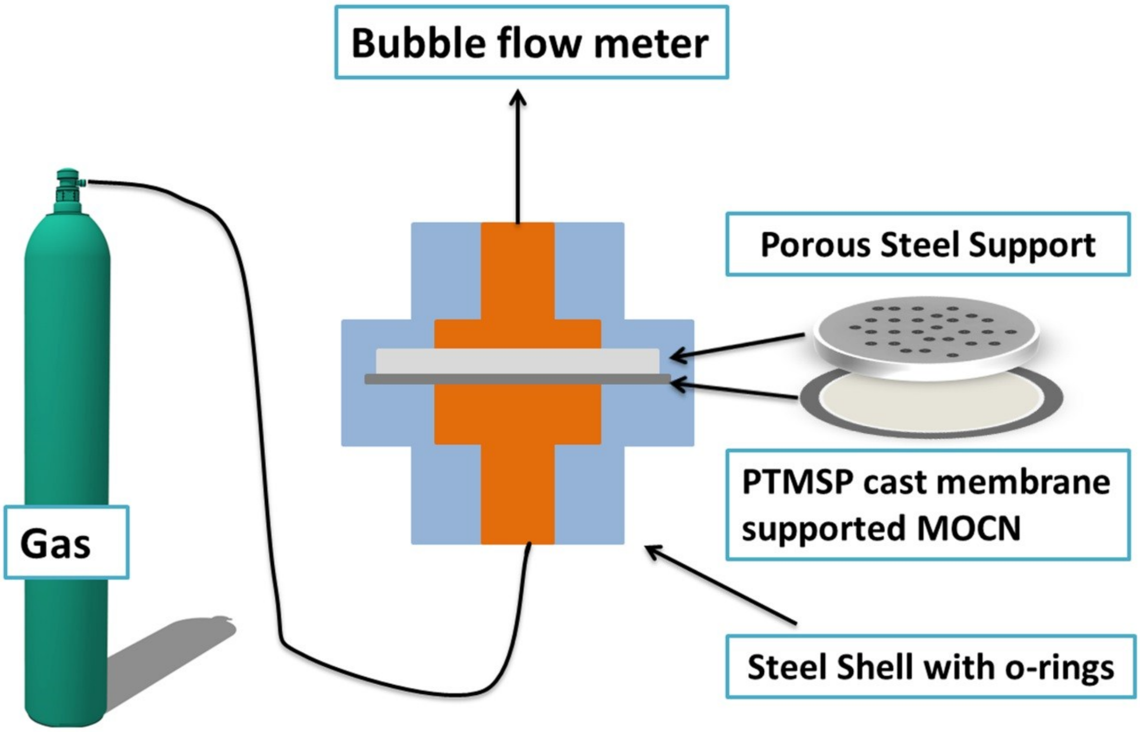

Figure S3. Schematic drawing of the house-constructed gas permeation cell operated in constant pressure mode.

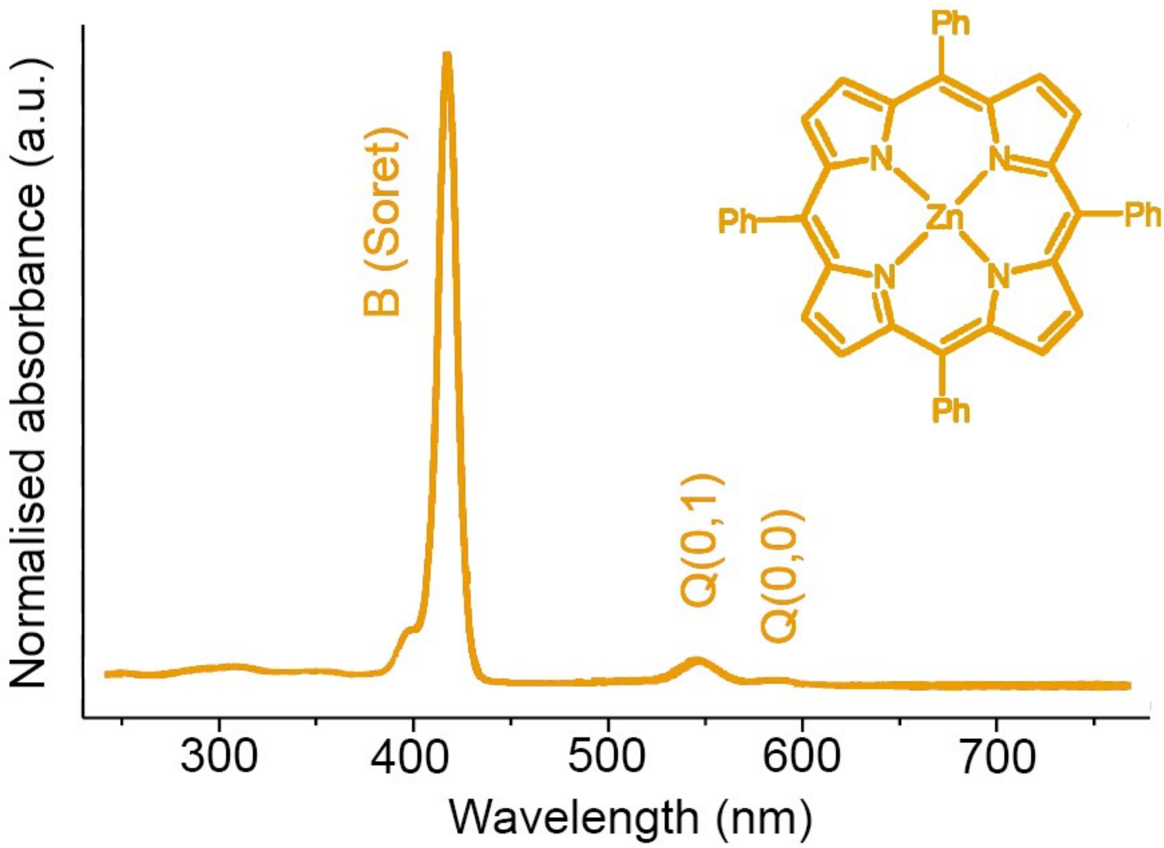

Figure S4. UV-vis absorption spectrum of zinc *meso*-tetraphenylporphyrin (ZnTPP) in *n*-hexane and chemical structure of ZnTPP.

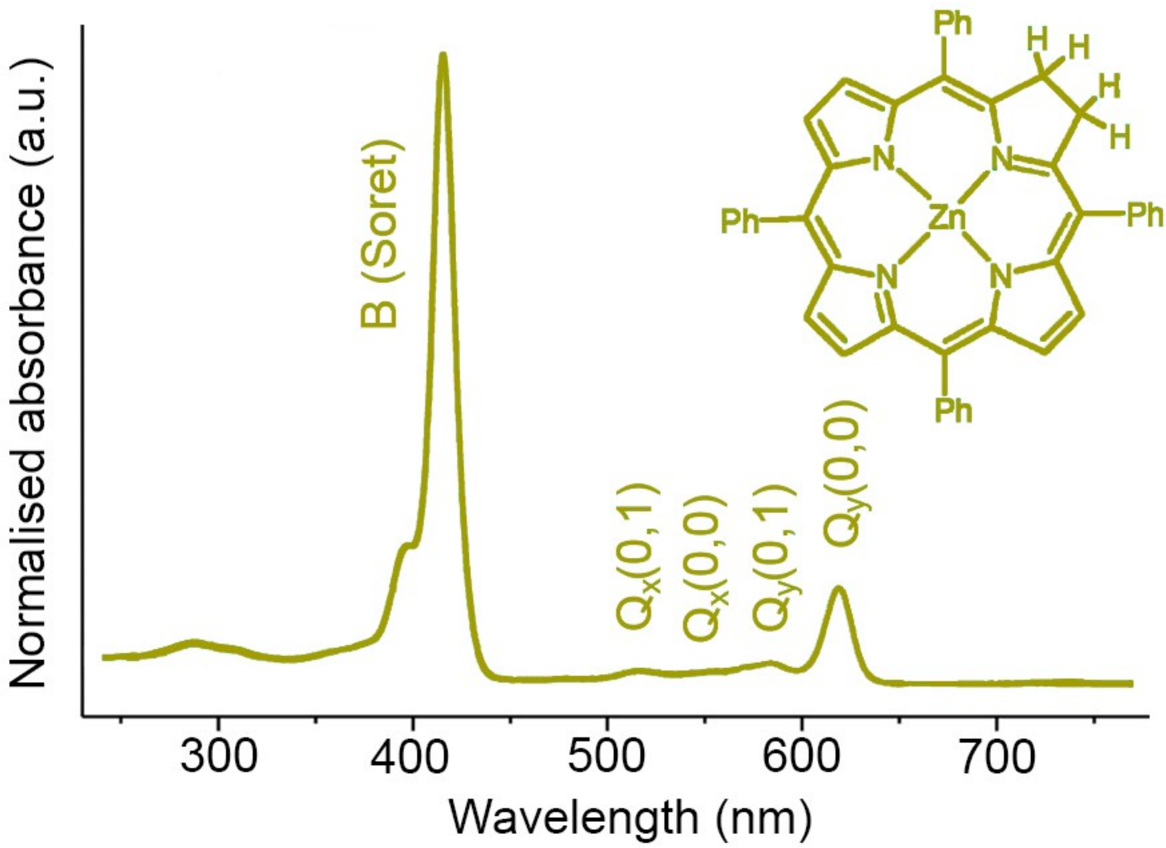

Figure S5. UV-vis absorption spectrum of zinc *meso*-tetraphenylchlorin (ZnTPC) in *n*-hexane and chemical structure of ZnTPC.

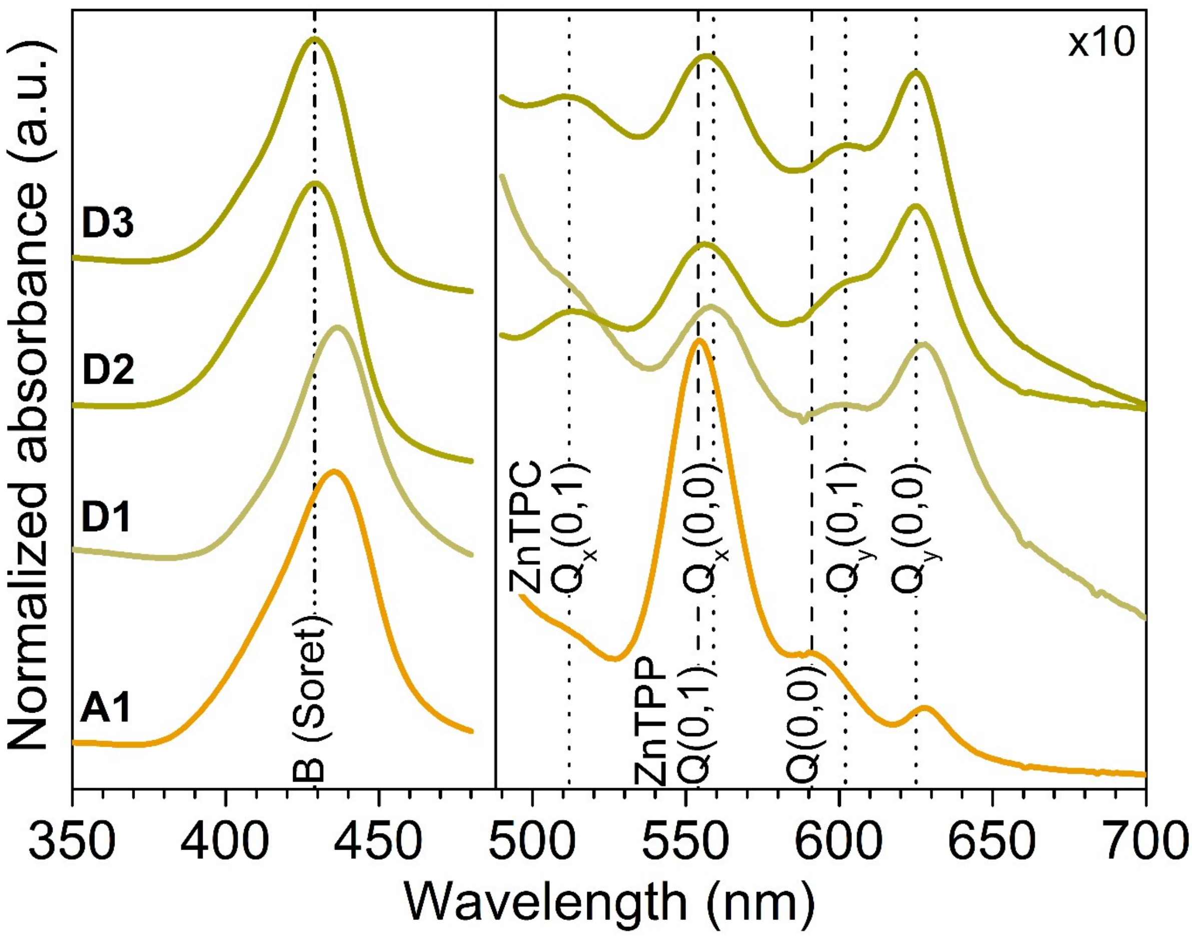

Figure S6. UV-vis absorption spectra of the thin films deposited on glass substrate from the evaporation of ZnTPP (condition A1) and from the PECVD (condition D1) and iPECVD reaction of ZnTPP without (condition D2) and with DVB (condition D3).

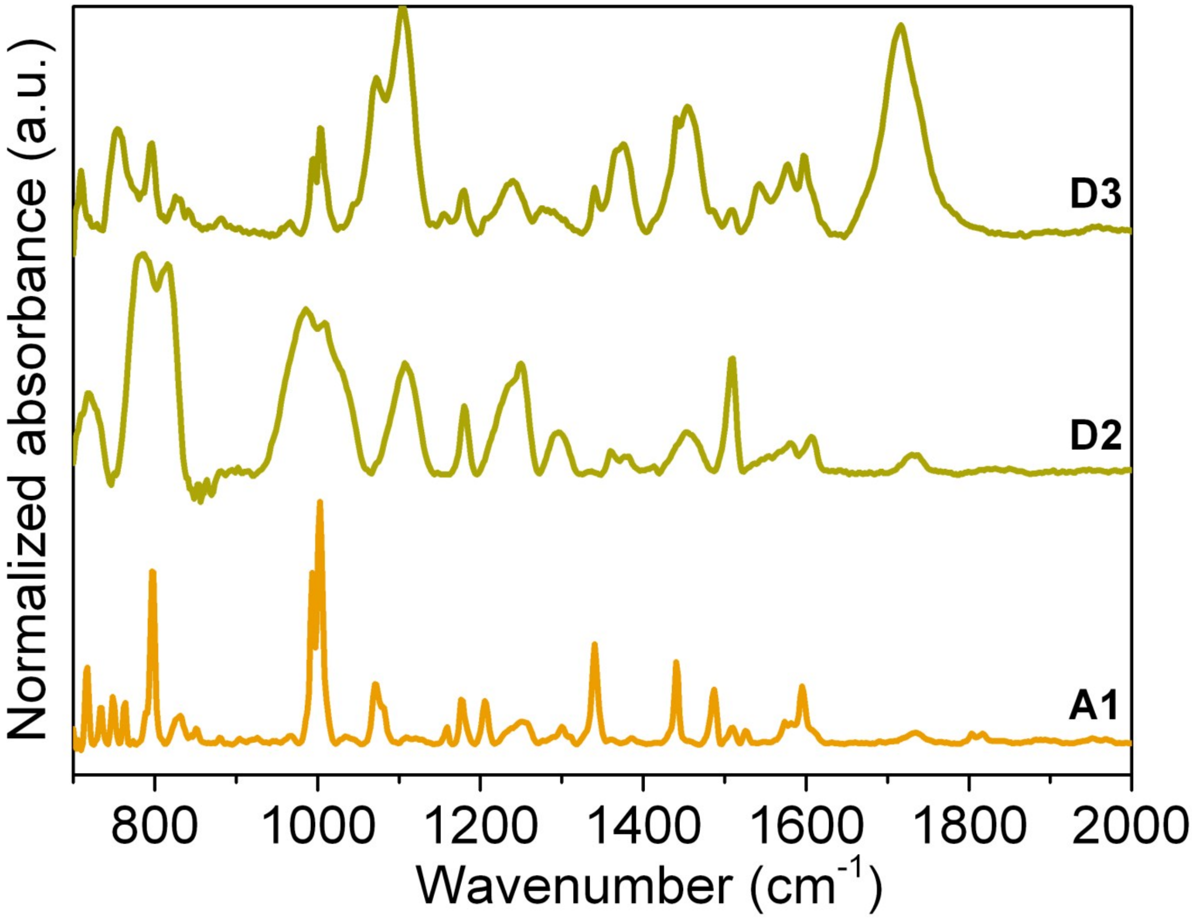

Figure S7. ATR-FTIR absorption spectra of the ZnTPP thin film prepared from the evaporation of ZnTPP (condition A1) and the P(ZnTPC) and P(DVB-co-ZnTPC) thin films prepared from the iPECVD reaction of ZnTPP without (condition D2) and with DVB (condition D3).

Table S1. Chemical composition of the thin films as measured by XPS.

		C (%)	Zn (%)	N (%)	O (%)
theoretical	**ZnTPP**	89.8	2.0	8.2	0
condition A1	**ZnTPP**	90.9	1.8	5.9	1.4
condition D2	**P(ZnTPC)**	90.1	1.6	4.9	3.4
condition D3	**P(DVB-co-ZnTPC)**	92.8	1.0	3.1	3.1
iPECVD at 20 W	**P(DVB)**	96.4	0	0	3.6
theoretical	**P(DVB)**	100	0	0	0

Table S2. Intensity retention of the Soret band of the thin films deposited on glass substrate after soaking for 1 hour in various solvents, *i.e.* water, methanol, toluene and chloroform.

		solvents			
		water	**methanol**	**toluene**	**chloroform**
condition A1	**ZnTPP**	90 %	0 %	0 %	0 %
condition D2	**P(ZnTPC)**	100 %	0 %	95 %	0 %
condition D3	**P(DVB-co-ZnTPC)**	100 %	50 %	100 %	25 %

Table S3. Observed gas barrier properties, from single gas permeation measurements,* of the pristine PTMSP membrane and of composite membranes prepared from PTMSP membranes coated by thin films with different thicknesses (*ca.* 20, 40 and 80 nm) deposited from conditions A1, D2 and D3.

		H_2 (GPU)	CO_2 (GPU)	O_2 (GPU)	N_2 (GPU)	CH_4 (GPU)
-	**PTMSP**	674	1395	394	266	666
condition A1	**ZnTPP/PTMSP**	540	198	195	205	268
condition D2	**P(ZnTPC)-20/PTMSP**	272	92.5	10.2	1.72	2.06
	P(ZnTPC)-40/PTMSP	139	68.1	8.23	1.01	0.972
	P(ZnTPC)-80/PTMSP	76.9	14.3	3.17	0.297	0.191
condition D3	**P(DVB-co-ZnTPC)-40/PTMSP**	68.3	16.8	4.04	0.459	0.329
	P(DVB-co-ZnTPC)-80/PTMSP	45.0	12.2	2.20	0.201	0.0818

*Permeances were measured at ambient temperature with upstream pressure set at 73.5 psig. The permeances were calculated by dividing the flow rate by the pressure gradient (73.5 psi) and by the area of the membrane (9.36 cm^2). Average values were obtained from 5 to 10 independent measurements on the same sample; the error in each case was ± 5 %. Each membrane listed was prepared, independently. 1 GPU = 10^{-6} $cm^3(STP).cm^{-2}.s^{-1}.cmHg^{-1}$.

Table S4. Gas selectivity, calculated from the single gas permeation measurements, for the pristine PTMSP membrane and of composite membranes prepared from PTMSP membranes coated by thin films with different thicknesses (*ca.* 20, 40 and 80 nm) deposited from conditions A1, D2 and D3.

		CO_2/CH_4	CO_2/N_2	O_2/N_2	H_2/CH_4	H_2/N_2
-	**PTMSP**	2.1	5.3	1.5	1.0	2.5
condition A1	**ZnTPP/PTMSP**	0.74	0.97	0.95	2.0	2.6
condition D2	**P(ZnTPC)-20/PTMSP**	45	54	6.0	133	160
	P(ZnTPC)-40/PTMSP	70	67	8.1	143	138
	P(ZnTPC)-80/PTMSP	75	49	11	402	260
condition D3	**P(DVB-co-ZnTPC)-40/PTMSP**	51	37	8.8	210	150
	P(DVB-co-ZnTPC)-80/PTMSP	150	61	11	550	224