Supporting information for

Metallodynameric membranes-toward the constitutional transport of gases

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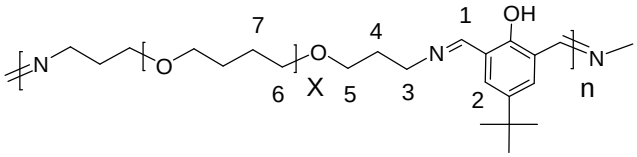
Materials and Methods: All reagents were obtained from Aldrich and used without further purification. All organic solutions were routinely dried by using sodium sulfate (Na_2SO_4). ^{1}H-NMR spectra were recorded on an ARX 300 MHz Bruker spectrometer in $CDCl_3$ using the residual solvent peak as reference. Thermogravimetric analysis (Hi-Res TGA 2950, TA Instruments, Nitrogen, 50-600 °C at 10°C/min) and Differential Scanning Calorimetry (DSC 2920 Modulated, TA Instruments) were used to evaluate thermal stability of the dynameric materials. FTIR measurements were performed with a Nicolet Nexus FT-IR spectrometer equipped with a ATR Diamant Golden Gate. X-ray powder diffraction measurements were performed with Cu-Kα radiation at 20°C using a Philips X'Pert Difractometer equipped with a Xcelerator detector.

General procedure for the synthesis of dynamers D_1-D_3:

1.0 moles of corresponding dialdehyde (0.20 g of 4-*tert*-Butyl-2,6-diformylphenol A**1**, 0.13 g of isophthaldehyde**, A2,** 0.13 g of 2,6-pyridinecarboxaldehyde**, A2)** and bis(3-aminopropyl) poly(tetrahydrofuran), poly*THF* **T** (1.07g, 1.0 moles), were solubilized in 250 ml of THF. The reaction mixture was vigorously stirred for overnight at reflux. The reaction mixtures were refluxed overnight under stirring and then evaporated. The resulted dynamers **D_1-D_3** were dryed in vaccum for 2 more days.

General procedure for the synthesis of metallodynameric MD_1Me-MD_3Me membrane films: 0.7 g of dynamer **D_1** to **D_3** is dissolved in 4 ml of THF, Then a methanolic solution of 0.06 g, $Zn(CH_3COO)_2$ or 0.106 g, $ZnTf_2$ or 0.1 g $CoTf_2$, or 0.1 g $Fe(BF_4)_2$, (0.5 eq or relative to the repetitive polymeric unit) is added drop by drop to the solution and the reaction mixture was vigorously stirred for 1 hour. The solution colour change instantaneously, reminiscent with the rapid formation of the metallodynamers **MD_1Me**-M**D_3Me**. The mixture was poured into a Teflon mould and dried slowly at room temperature for one day and at 60°C for 3 days. The thickness of self-standing/non-supported membrane was in the range of 300 to 600 µm.

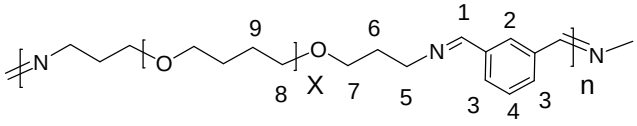


D1: ^{1}H-NMR (300MHz, $CDCl_3$) : 8,49 (él, 2H, CH=N) ; 7,57 (él, 2H, CH-2) ; 3,55 (t, 4H, CH-5) ; 3,41 (t, 4H, CH-3); 3,39 (él, 5'H, CH-6) ; 1,92 (t, 4H, CH-4) ; 1,53 (él, 54H, CH-7) ; 1,14-1,24 (m, 9H, tBu). M= 1270,24 g.mol^{-1} IR (cm^{-1}): 2937, 2852, 2795, 1636.1598, 1465, 1446, 1364, 1206,1103. DSC 1st cycle : Tg (°C) : -68,5 ; Tc= -14,80, Tm (°C): 9,23; DHm (J/g): 23,06. DSC 2nd cycle : Tg (°C) : -68,25 ; Tc= -24,11, Tm (°C): 10,16; DHm (J/g): 30,62

MD1Zn: ^{1}H-NMR (300MHz, $CDCl_3$) : 8,32-8,18 (d él, 2H, CH=N) ; 7,42 (br, 2H, CH-2) ; 3.53 (él, 4H, CH-5) ; 3,22 (él, 58H, CH-6,3) ; 1,76-1,62 (m, 5,5H, CH-4, CH_3-COO^-) ; 1,41 (él, 54H, CH-7); 1.1 (m, 9H, tBu). IR (cm^{-1}): 2933, 2652, 2794, 1609, 1581, 1412, 1363, 1232, 1206, 1104, 1023, 841, 777, 667, 614, 498. DSC 1st cycle : Tg (°C) : -68,25; 29,50; DSC 2nd cycle : Tg (°C) : -69,51; 20,04

MD1Co IR (cm^{-1}): 2938, 2853, 2796, 1655, 1629, 1541, 1482, 1447, 1365, 1290, 1236, 1210, 1098, 840, 763; DSC 1er cycle : Tg (°C) : -74.1 ; Tm (°C): 133.7; DHm (J/g): 6.0
DSC 2^{em} cycle : Tg (°C) : -74.9 ; Tm (°C): ND; DHm (J/g): ND

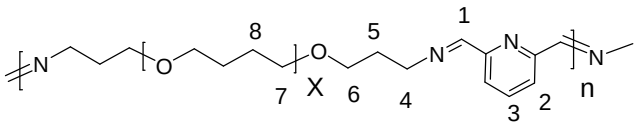
MD1Fe: IR (cm^{-1}): 2939, 2854, 2797, 1645, 1582, 1528, 1482, 1366, 1235, 1208, 1098, 839, 522; DSC 1er cycle : Tg (°C) : -74.47 ; Tm (°C): 136.8-255.1; DHm (J/g): 9.7. DSC 2^{em} cycle : Tg (°C) : -74.3 ; Tm (°C):142.7-255.1; DHm (J/g): 10



D2: ^{1}H-NMR (300MHz, $CDCl_3$): 8.3 (él, 2H, CH=N) ; 8.0 (él, 1H, CH-2) ; 7.7 (él, 2H, CH-3) ;7.4 (él, 1H, CH-4) ; 3.7 (él, 4H, CH-7) 3.5 (él, 58H, CH-8,5) ; 2 (él, 4H, CH-6) ; 1.5 (él, 54H, CH-9). IR (cm^{-1}): 2937, 2852, 2795, 2740, 1647, 1482, 1446, 1366, 1241,1208, 1104, 967. DSC 1er cycle : Tg (°C) : -68.4 ; Tm (°C): 11.7; DHm (J/g): 45.2.

MD2Zn IR (cm-1): 2941, 2861, 2802, 1646, 1490, 1371, 1250, 1209, 1107, 1029, 994,745, 639, 564; DSC 1er cycle : Tg (°C) : -73.5 ; Tm (°C): ND; DHm (J/g): ND; DSC 2^{em} cycle : Tg (°C) : -75.1 ; Tm (°C): 9.25; DHm (J/g): 10.4

MD2Co: DSC 1er cycle : Tg (°C) : -77.1 ; Tm (°C): 10; DHm (J/g): 6.6
MD2Fe: IR (cm^{-1}): 2939, 2855, 2797, 1732, 1673, 1446, 1370, 1242, 1208, 1101, 708, 496
DSC 1er cycle : Tg (°C) : -74.7 ; Tm (°C): 6.9; DHm (J/g): 13.5



D3: ^{1}H-NMR (300MHz, $CDCl_3$): 8.4 (s, 2H, CH=N) ; 8.0 (d, 2H, CH-2) ; 7.8 (t, 2H, CH-3) ; 3.7(t, 4H, CH-6) ; 3.5 (t, 4H, CH-4) 3.5 (él, 54H, CH-7) ; 1,9 (m, 4H, CH-5) ; 1.6 (él, 54H, CH-8) ; IR (cm^{-1}): 2937, 2852, 2795, 1647, 1446, 1366, 1240, 1209, 1104, 967. DSC 1er cycle : Tg (°C) : -66.9 ; Tm (°C): 8.4; DHm (J/g): 32.0; DSC 2^{em} cycle : Tg (°C) : -63.8 ; Tm (°C): 10.75; DHm (J/g): 34.5.

MD3Zn ^{1}H-NMR (300MHz, $CDCl_3$) : 8.4 (él, 2H, CH=N) ; 8.2 (t, 1H, CH-3) ; 7.9 (d, 2H, CH-2) ; 3.7(t, 4H, CH-4) ; 3.2-3.7 (él, 58H, CH-4,7) ; 2 (él, 4H, CH-5) ; 1.5 (él, 54H, CH-8). IR (cm^{-1}): 2939, 2855, 2797, 1641, 1592, 1468, 1370, 1278, 1243, 1224, 1160, 1104, 1028, 812, 637, 577; DSC 1er cycle : Tg (°C) : -76.4 ; Tm (°C): ND; DHm (J/g): ND; DSC 2^{em} cycle : Tg (°C) : -75.5 ; Tm (°C): 16. 5; DHm (J/g): 34.4

MD3Fe: **IR (cm^{-1}):** 2934, 2853, 2796, 1731, 1658, 1446, 1367, 1239, 1102, 747, 520.

MD3Co: IR (cm^{-1}): 2938, 2853, 2795, 1641, 1446, 1367, 1241, 1208, 1099, 763, 521. DSC 1er cycle: Tg (°C) : -73.8; DSC 2^{em} cycle : Tg (°C) : -73.8

MD3Ag: IR (cm^{-1}): 2936, 2851, 2795, 1649, 1586, 1446, 1366, 1242, 1208, 1102, 826
DSC 1er cycle: Tg (°C) : -73.8 ; Tm (°C): 80.4; DHm (J/g): 6.0; DSC 2^{em} cycle : Tg (°C) : -74.6 ; Tm (°C): 76. 9; DHm (J/g): 6.2

Gel Permeation Chromatography: The molar mass and the polydispersity of resulted dynamers have been determined by using GPC method and different polystyrene DMF solutions for calibration. The results presented in Table 1S, show a mass around 10000 g/mol and a polydispersity around 1.

Table 1S. Molar mass M_n and polydispersity number for the dynamers **D1**-**D3**

Dynamers	M_n	PD
D1	12634	1
D2	13889	1,56
D3	8097	1,18

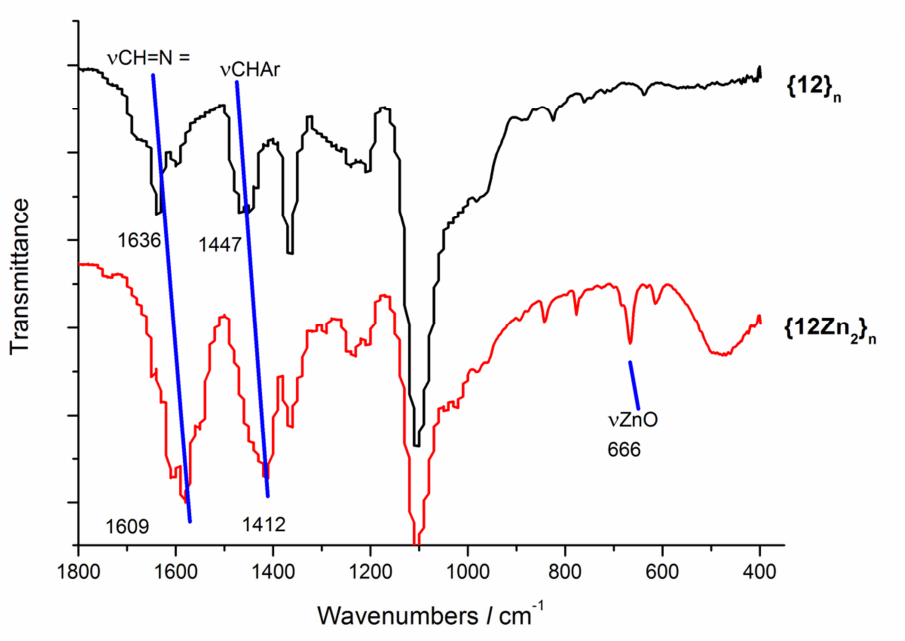


Figure 1S. FTIR spectra of dynameric materials **D1** and **MD1Zn**

Table 2S. DSC analysis of the dynameric as measured at 10°C/min under nitrogen.

Membrane	T_g (°C)
D1	-68,5
MD1Zn	-67,31
MD1Fe	-74,47
MD1Co	-74,14
D2	-68,4
MD2Zn	-73,52
MD2Fe	-74,7
MD2Co	-77,1
D3	-66,9
MD3Zn	-76,38
MD3Fe	-73,83
MD3Co	-73,83

Gas permeation and sorption experiments: Permeation experiments were performed by using permeability apparatus at constant temperature (298K).The equipment consisted on a cell with two compartments separated by the tested membrane. Each membrane was outgased for at least 48 hours at high vacuum (1.0×10^{-5} Pa). The pressure in the upstream compartment was 1.6×10^{5} Pa. (with a constant volume of 5.25×10^{-5} m^3 or 0.83 10^{-5} m^3). The variation pressure in downstream compartment was measured. The slope dP_2/dt of the obtained curve, presents, (in the case of CO_2) transitional and pseudo steady state regions.

The equation (1,2) obtained from the mathematical treatment for thin films based on Fick's second law lead to the permeability coefficient and diffusion coefficient:

$$Pe = S.D = Ve/ARTP_1 (dP_2/dt) \ (mol(STP).m^{-1}.s^{-1}.Pa^{-1}) \qquad (1)$$

Pe : permeability coefficient $(mol.m^{-1}.s^{-1}.Pa^{-1})$
V : upstream volume (5.25×10^{-5} m^3 or $0.83\ 10^{-5}$ m^3)
e : thickness (m)
A : Area of the membrane (m^2)
R : constant of ideal gas (R = 8,314 $J.mol^{-1}.K^{-1}$)
T : temperature (T = 298 K)
P_1 : upstream pressure ($P_1 = 1.6.10^5$ Pa)

$$D = e^2/6\Theta \qquad (2)$$

Θ= extrapolation of the linear steady state on the linear axis.

The second Fick law give the mass transfer coefficient Q that can be simplified at infinite time. $Qt \to \infty = \frac{DC1}{l}(t - l2\frac{l2}{6D})$. The extrapolation of the linear steady state (θ) on the time axis give the diffusion coefficient calculated from this time lag method: $D_{timelag}$: $D = \frac{l2}{6\theta}$

The values of solubility coefficients obtained from permeability experiments (by the time lag, $S_{time\text{-}lag}$) and experimental Pe = D.S (D_{calc}) are reported in Figure 2S.

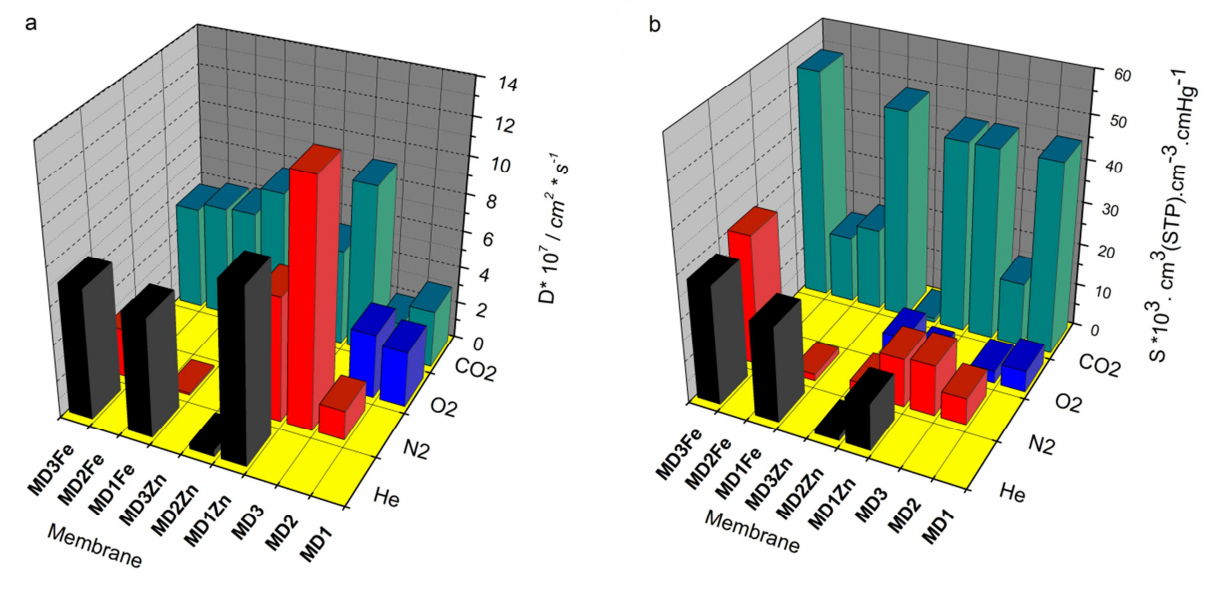


Figure 2S. Diffusion $D_{time\text{-}lag}$ and Solubility $S_{time\text{-}lag}$ coefficients for, calculated from time lag method.