Supporting information for

Metallodynameric membranes-are metallic ions facilitating the transport of CO$_2$?

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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$_2$SO$_4$). ^{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. SEM images were obtained with a Hitachi S-4500 apparatus, under a tension of 0.5-30 kV. 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 dynamer {12}$_n$:

4-*tert*-Butyl-2,6-diformylphenol (0.20g, 1.0 moles), **1** and bis(3-aminopropyl) poly(tetrahydrofuran), poly*THF* **2** (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 dynamer **{12}$_n$** was dried in vaccum for 2 more days.

General procedure for the synthesis of metallodynameric {12Zn$_x$}$_n$ x=0.5, 1, 2 membrane films: 0.7 g of dynamer **{12}$_n$** is dissolved in 4 ml of THF, Then a methanolic solution of Zn(CH$_3$COO)$_2$ (0.5 eq (0.06g), 1eq (0.12g) or 2eq (0.24g) 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 **{12Zn$_x$}$_n$** x=0.5, 1, 2. 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.
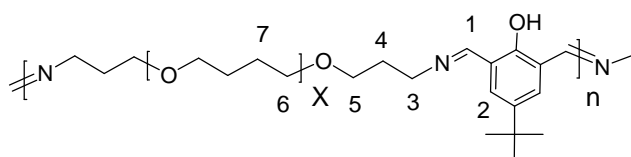
{12}$_n$: ^{1}H-NMR (300MHz, CDCl$_3$) : 8,49 (él, 2H, CH=N) ; 7,57 (él, 2H, CH-2) ; 3,55 (t, 4H, CH-5) ; 3,41 (t, 4H, CH-3); 3,39 (él, 5'H, CH-6) ; 1,92 (t, 4H, CH-4) ; 1,53 (él, 54H, CH-7) ; 1,14-1,24 (m, 9H, tBu). M= 1270,24 g.mol^{-1} IR (cm^{-1}): 2937, 2852, 2795, 1636.1598, 1465, 1446, 1364, 1206,1103. 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

{12Zn$_{0.5}$}$_n$ ^{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

{12Zn}$_n$(AcO)$_n$ ^{1}H-NMR (300MHz, CDCl$_3$) : 8,11 (él, 2H, CH=N) ; 7,45 and 7,31 (d él, 2H, CH-2) ; 3,51 (él, 4H, CH-5) ; 3,28 (él, 58H, CH-6,3) ; 1,92 (s, 3H, CH$_3$-COO$^-$) ; 1,82 (él, 4H, CH-4) ; 1,47 (él, 54H, CH-7); 1,11 (m, 9H, tBu). IR (cm^{-1}): 2933, 2652, 2794, 1609, 1581, 1412, 1363, 1232, 1206, 1104, 1023, 841, 777, 667, 614, 498
DSC 1er cycle : Tg (°C) : -67,30; 12,41 ; DSC 2ème cycle: Tg (°C) : -67,81; 7,37

{12Zn$_2$}$_n$(AcO)$_{3n}$ ^{1}H-NMR (300MHz, CDCl$_3$) : 8,13 (él, 2H, CH=N) ; 7,25 (él, 2H, CH-2) ; 3,70 (él, 4H, CH-5) ; 3,40 (él, 58H, CH-6,3) ; 1,90 (s, 6H, CH$_3$-COO$^-$) ; 1,82 (él, 4H, CH-4) ; 1,51 (él, 54H, CH-7) 1,20 (m, 9H, tBu).IR (cm^{-1}): 2933, 2652, 2794, 1609, 1581, 1412, 1363, 1232, 1206, 1104, 1023, 841, 777, 667, 614, 498
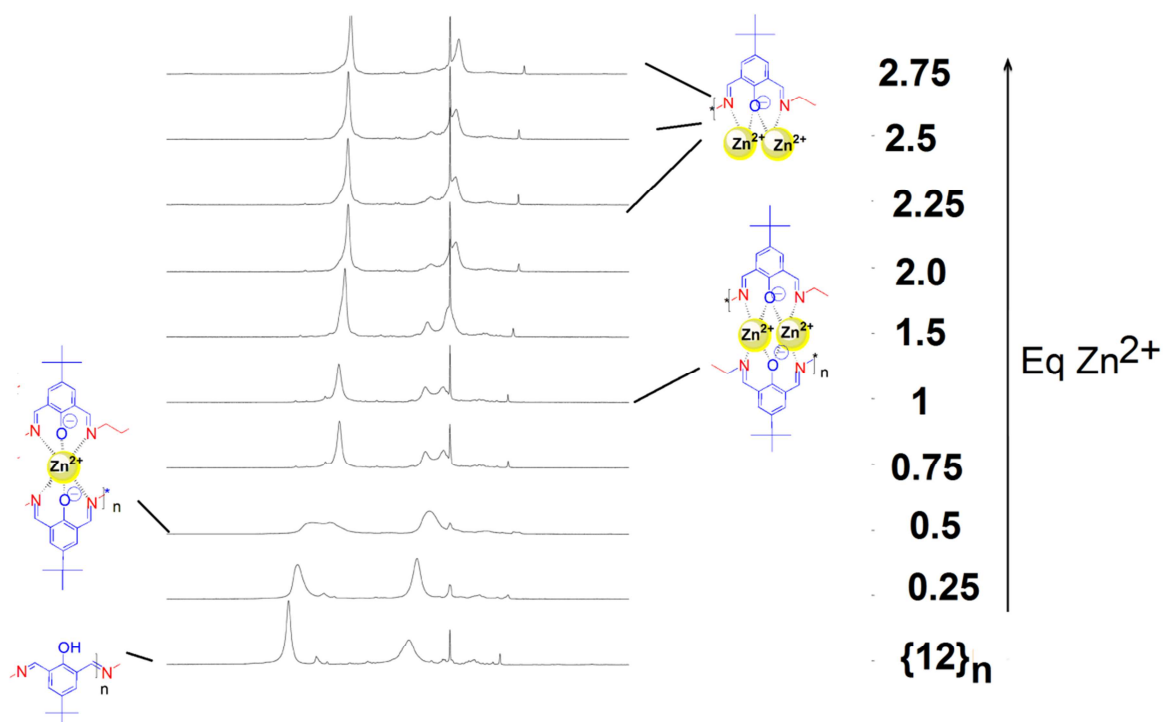DSC 1er cycle : Tg (°C) : -63,77; 129,97 ; DSC 2ème cycle : Tg (°C) : -65,28; 104,24

Figure 1S. Aromatic /imine region of the ^{1}H-NMR spectra obtained on the titration of a solution of dynamer $\{12\}_n$ in CDCl$_3$ by a solution of Zn^{2+} in CH$_3$CN .
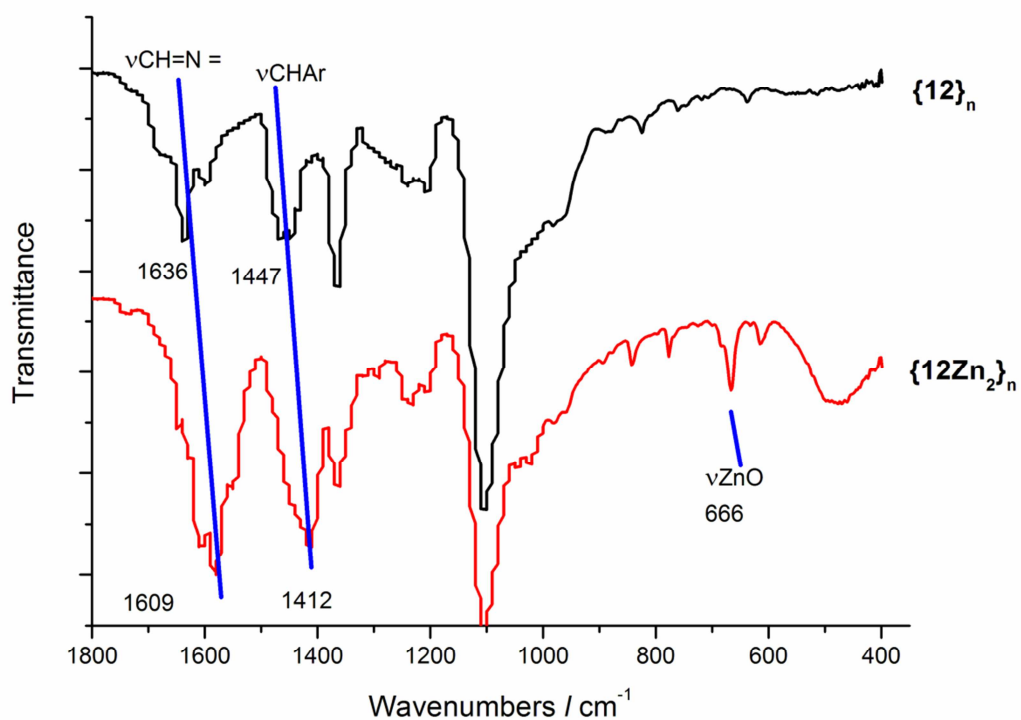

Figure 2S. FTIR spectra of dynameric materials $\{12\}_n$ and $\{12Zn_2\}_n$
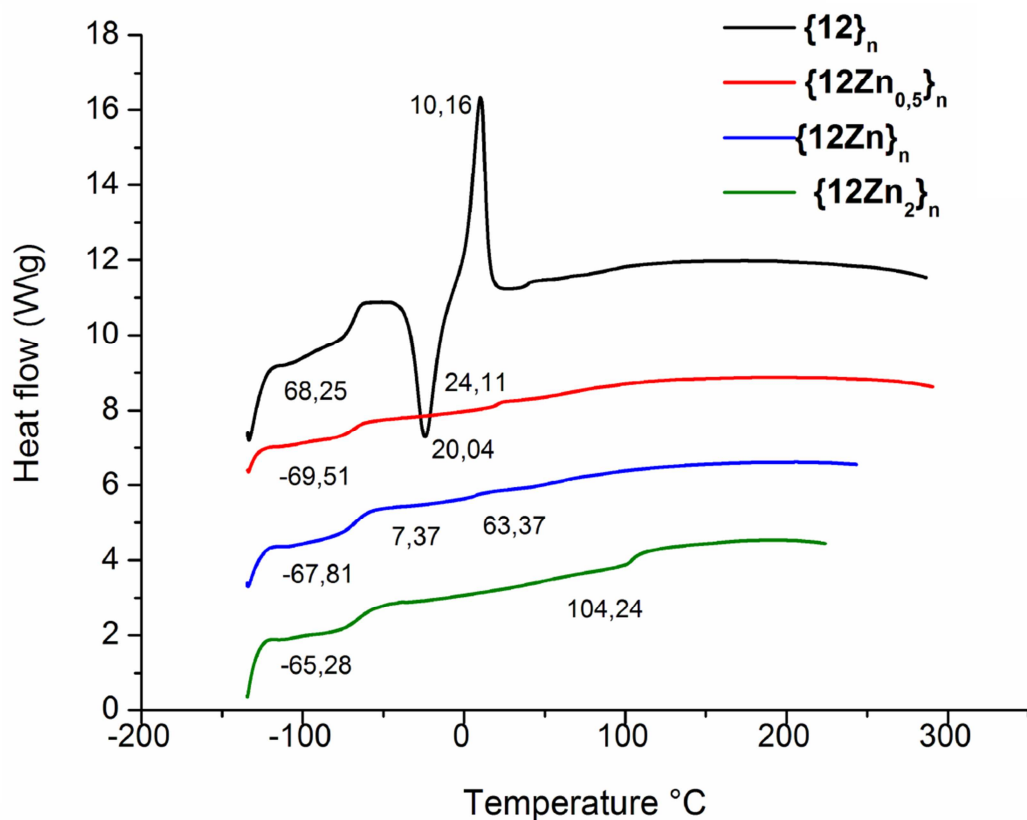
Figure 3S. DSC traces of the dynameric as measured at 10°C/min under nitrogen.

Table 1S. DSC analysis of the dynameric as measured at 10°C/min under nitrogen.

Membrane	Tg 1st cycle	Tg 2nd cycle	Tc 1st cycle	Tc 2nd cycle	Tm 1st cycle	Tm 2nd cycle
{12}$_n$	-68,25	-68,25	-14,80	-24,11	9,23	10,16
{12Zn$_{0.5}$}$_n$	-68,25 / 29,50	-69,15 / 20,04	-	-	-	-
{12Zn}$_n$	-67,30 / 12,41 / 62,36	-67,81 / 7,37 / 63,37	-	-	-	-
{12Zn$_2$}$_n$	-63,77 / 129,97	-65,28 / 104,24	-	-	-	-

Water swelling experiments: In order to estimate the free-volume increase as function as the content of zinc metal ions, the swelling of films was measured in water (SWR). The swelling ratio was calculated as following: SWR= $m-m_0/m_0$ x100, where m and m_0 are the the weight of the dry and wet film, respectively.

Figure 4S shows the evolution of SWR as function of the Zn^{2+} content. The swelling ratio increases abruptly from 26% to 420% at 1.0 equivalent of Zn^{2+}, indicating a strong increase of free volume and sorption properties of metallodynameric films. This SWR is then, almost stable for 1 and 2 equivalent of Zn^{2+}.
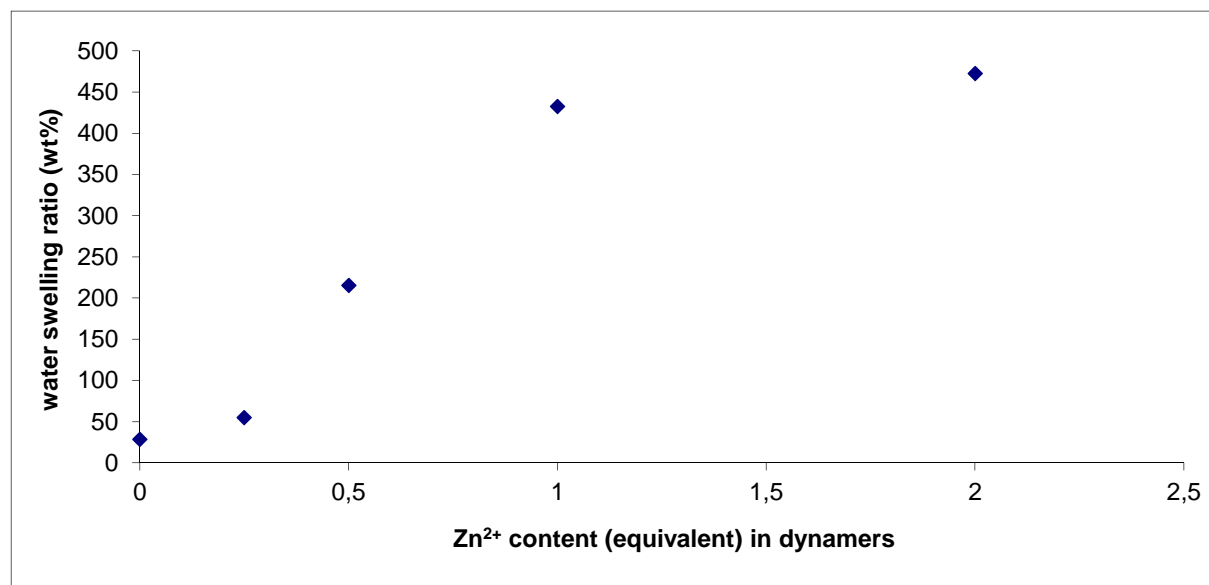

Figure 4S. Evolution of the swelling ratio vs. the Zn^{2+} content for dynameric membranes

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:

$$Pe= S.D= Ve/ARTP_1 \ (dP_2/dt) \ (mol(STP).m^{-1}.s^{-1}.Pa^{-1}) \hspace{2cm} (1)$$

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)

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

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

The sorption Analysis was realized in a Cahn microbalance at $1.6.10^5$ Pa of gas pressure at 298K. The soption isotherms were performed by recording the weight after contact with carbon dioxide the coefficient sorption is calculated from the equation bellow:

$$S = \frac{VCO2 sorbate}{Vpolymer} \ x \ \frac{1}{P} \ \text{cm}^3 \ CO_2 \ (STP). \ \text{cm}^3 \ \text{polymer.} \ \text{cm}^{-1}.\text{Hg T}$$

The values of solubility coefficients obtained from permeability experiments (by the time lag, $S_{time-lag}$) and experimental Pe = D.S (*D*calc) are reported in table. We observe an excellent agreement between the calculated and experimental diffusion coefficients for CO_2.

Table 2S: Solubility coefficient for CO_2, calculated from time lag $S_{time-lag}$ and experimental S'.

	$S_{time-lag} \ 10^{-3}$ (cm^3(STP)cm^{3}cm^{-1}Hg)	S' 10^{-3} (cm^3(STP)cm^{-3}cm^{-1}Hg)
{12}$_n$	13,55	7.25
{12Zn$_{0.5}$}$_n$	13,11	12.1
{12Zn}$_n$	13.9	14.5
{12Zn$_2$}$_n$	20,00	18.8