

Supporting Information

Synthesis of novel Co(II) complexed bipyrimidine polyimide and preparation of thin film composite membranes

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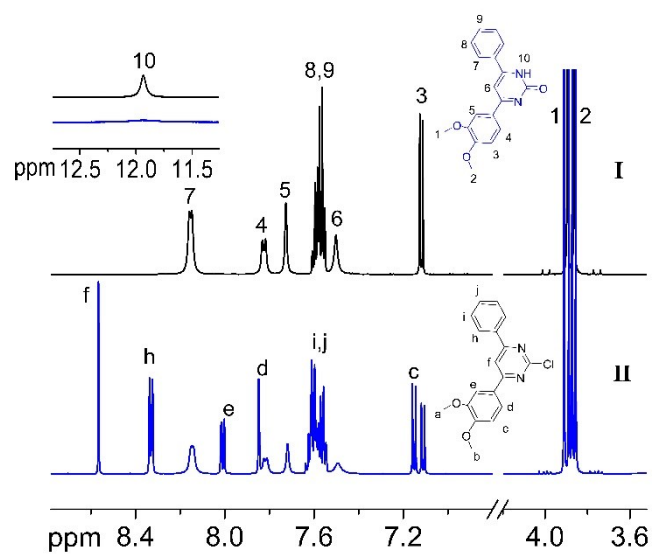


Fig. S1 ^1H NMR spectra of compound I and compound VI.

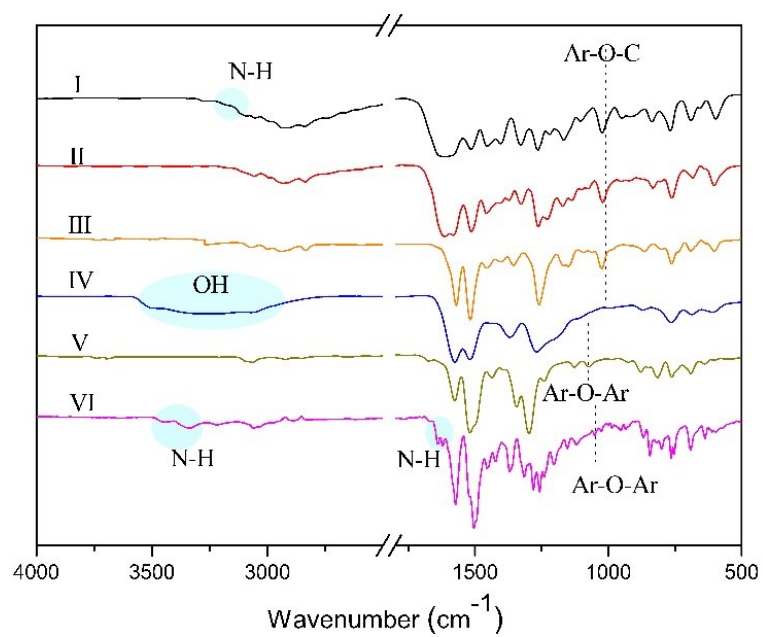


Fig. S2 FTIR spectra of compounds I-VI.

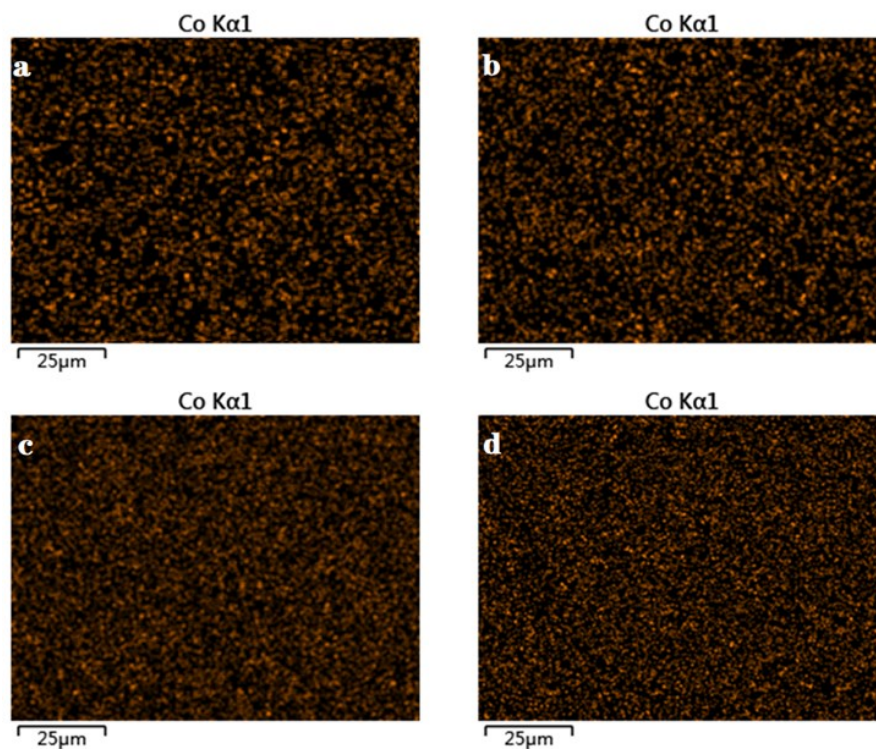


Fig.S3 Surface EDS mapping images: (a) DMD-CPI-3.0, (b) DMD-CPI-10, (c) DMD-CPI-15, (d) DMD-CPI-20.

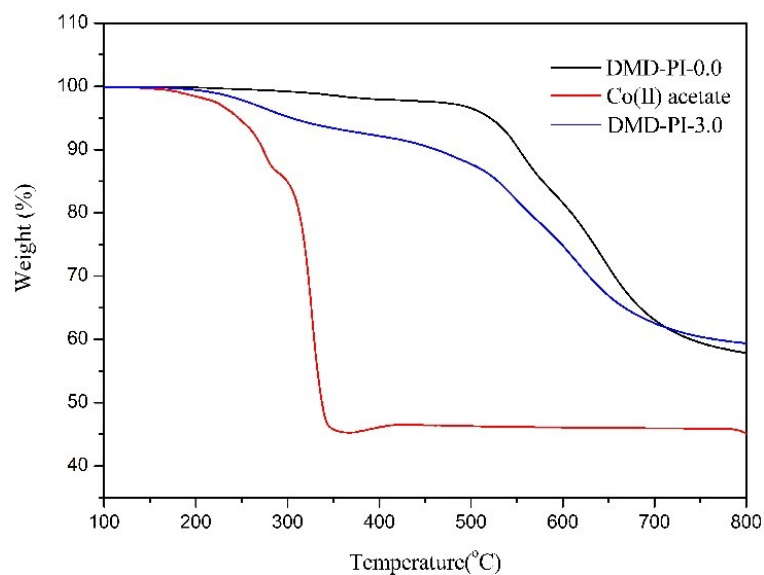


Fig. S4 TGA curves of DMD-PI-0.0, DMD-PI-3.0 and Co(II) acetate in N_2 .

The thermal resistance of a membranes can meet the requirements of at elevated temperatures. The thermal performance of DMD-PI-x was estimated by DSC, TGA

from two perspectives. Seen from **Fig. S4**, the 5% weight temperature loss of DMD-PI-0.0 was 519.1°C, and the residual weight retentions at 800°C was 58.01% in N₂. The above proves that DMD-PI-0.0 has remarkable thermal stability. The initial analysis of 2.1% weight loss at 405°C was presumed to be caused by the movement of the segment and the evaporation of excess solvent. In addition, the 2.1% weight loss of dmd-PI-0.0 at 405 °C was initially speculated to be caused by segment movement and volatile residual solvents.

Cobalt acetate mainly decomposes in three steps in nitrogen. As the first step begins to lose weight (loss of crystal water) at 140°C, and the weight loss rate accumulates 13.70%. Step 2 weightlessness is at 290°C. Cobalt acetate first generates cobalt oxalate, then decomposes into Co₃O₄, and eventually becomes CoO, with a cumulative weight loss rate of 86.24%. In the third step, the weight increased by 0.97% from 365oC to 425°C because CoO was re-oxidized to Co₃O₄.

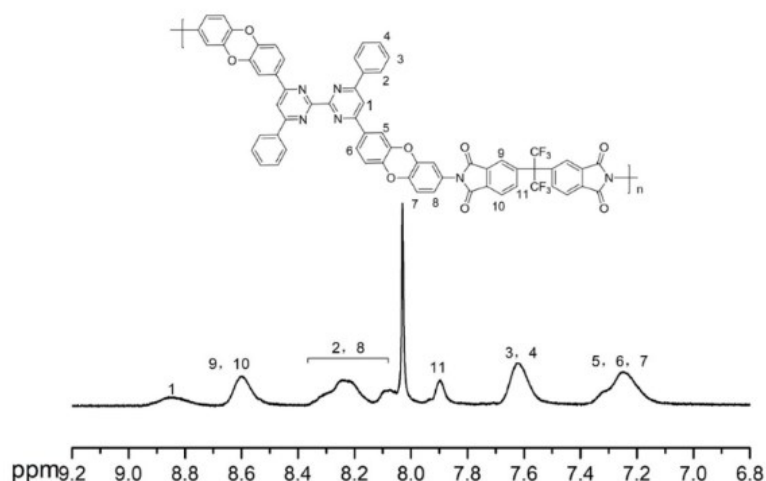
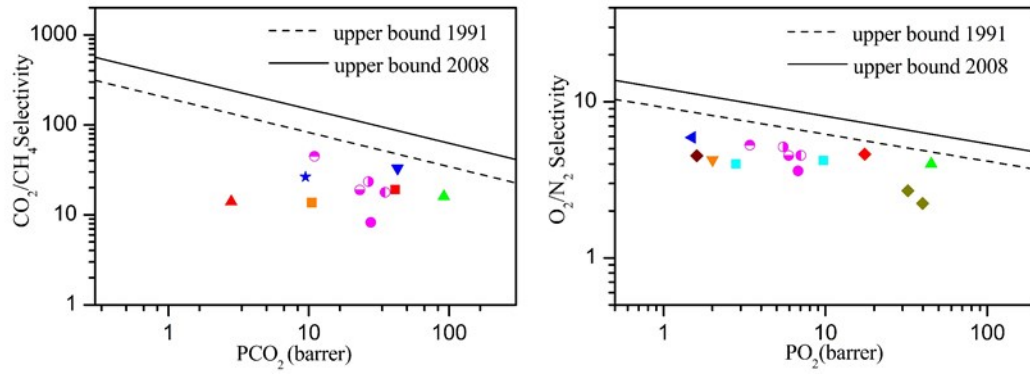


Fig. S5 ¹H NMR spectrum of DMD-PI-0.0.

Table.S1 Solubility of DMD-PI-X.

Membranes	CH ₃ OH	CHCl ₃	NMP	DMAc	DMF	DMSO
DMD-PI-0.0	-	-	++	++	++	+
DMD-PI-3.0	-	-	+	+	+	-
DMD-PI-10	-	-	-	-	-	-
DMD-PI-15	-	-	-	-	-	-
DMD-PI-20	-	-	-	-	-	-

DMAc is N, N-dimethylacetamide; DMF is N, N-dimethylformamide; NMP is Nmethyl-2-pyrrolidone; DMSO is Dimethyl sulfoxide; DMSO is Dimethyl sulfoxide; CHCl₃ is chloroform. ++, soluble at room temperature; +, partial soluble; -, insoluble.

**Fig.S6** Robeson's upper-bound relevant to five TCFMs for CO₂/CH₄ and O₂/N₂.

The purple circle graphic represents DMD-PI-X (○: DMD-PI-15, ○: DMD-PI-20, ○: DMD-PI-10, ○: DMD-PI-3.0, ○: DMD-PI-0.0), others are references(▲:¹, ★:², ■:³, ▼:⁴, ■:⁵, ▲:⁶, ▲:⁷, ◆:⁸, ▼:⁹, ■:¹⁰, ◆:¹¹, ◆:¹².)

Table S2 Gas permeability and ideal selectivity of DMD-CPI-15 and other analogous polymer membranes from reference works.

Polymer	Support layer	Filler	Gas separation	Gas Permeance	Selectivity	Ref.
Polyimide ^a	Alumina hydrate	MWCNT	CO ₂ /CH ₄	CO ₂ : 11 GPU	CO ₂ /CH ₄ = 9	13
Polyimide ^b	Carbon support	CMS	O ₂ /N ₂	O ₂ : 45 Barrer	O ₂ /N ₂ = 4	6
			CO ₂ /CH ₄	N ₂ : 11.2 Barrer	CO ₂ /CH ₄ = 16	
			CO ₂ /N ₂		CO ₂ /N ₂ = 9	
Polyimide ^c	-	TiO ₂	CO ₂ /CH ₄	CO ₂ : 92 CO ₂ :15.9 Barrer	CO ₂ /CH ₄ =59.6	14
Polyimide ^d	-	SiO ₂	CO ₂ /N ₂	CO ₂ :0.86 Barrer	CO ₂ /N ₂ =28.67	15
			O ₂ /N ₂	O ₂ : 0.32 Barrer	O ₂ /N ₂ =11.33	
				N ₂ : 0.03 Barrer		
Polyimide ^e	Alumina	ZIF 8	CO ₂ /N ₂	CO ₂ :72 GPU	CO ₂ /N ₂ =7.2	16
				N ₂ : 10 GPU		
Polyimide ^f	-	Co(acac) ₃	O ₂ /N ₂	O ₂ : 14.7 Barrer	O ₂ /N ₂ =5.01	11
Pebax_1657	PAN	C60(OH) ₂₄	CO ₂ /CH ₄	CO ₂ :338 GPU	CO ₂ /CH ₄ = 41	17
			CO ₂ /N ₂	CH ₄ : 8.24 GPU	CO ₂ /N ₂ = 16	
				N ₂ : 21.1		

GPU						
Pebax	PVDF	ZIF 8	CO ₂ /CH ₄ CO ₂ /N ₂	CO ₂ :189 GPU CH ₄ : 15.75GPU N ₂ : 8.22 GPU	CO ₂ /N ₂ =23 CO ₂ /CH ₄ =12	18
Phenolic resin	Alumina	Carbon/SAPO-34	CO ₂ /CH ₄ CO ₂ /N ₂	CO ₂ : 14 GPU CH ₄ : 0.28 GPU N ₂ : 0.9 GPU	CO ₂ /N ₂ =15.55 CO ₂ /CH ₄ = 50	19
Polyimide	Alumina	15wt% Co(AC) ₃	O ₂ /N ₂ CO ₂ /CH ₄ CO ₂ /N ₂	O ₂ : 6.82 GPU N ₂ : 1.296 GPU CO ₂ : 21.95 GPU CH ₄ : 0.49 GPU	O ₂ /N ₂ = 5.27 CO ₂ /CH ₄ =44.79 CO ₂ /N ₂ = 28.45	This work

Notes and references

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