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Supporting information

Non-thermal polyimidization reaction using base-ionic liquid medium as a dual catalyst-solvent

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Materials

Table S1 Chemicals and reagents

Reagent	Supplier	Purity
PMDA	Boshan Hengtai Chem.	98%
ODA	Guansen Insulation Products	≥ 99.5%
IL		
[C_2mim][OAc]	BASF	≥ 95%
[C_4mim][OAc]	BASF	≥ 95%
[C_4mim][PF_6]	Shanghai Chenjie Chem.	≥ 99%
[C_4mim][BF_4]	Shanghai Chenjie Chem.	≥ 99%
[C_2mim][Et_2PO_4]	Sigma-Aldrich (China)	≥ 98%
[Cho][$C_2H_5CO_2$]	Sigma-Aldrich (China)	≥ 96%
Base		
DIPEA	Shanghai Ziye Chem. Eng.	99.9%
pyridine	Sigma-Aldrich (China)	99.8%
KOtBu	Energy Chem.	98%
DABCO	Sigma-Aldrich (China)	≥99%

General Procedures

All reagents were lyophilized overnight before use. 1 equivalent PMDA (3.00 mol% mol/L) and 1 equivalent ODA (3.00 mol%) were dissolved in IL and stirred under argon protection at room temperature. Base was added subsequently into the solution. The crude product was filtered out, washed 5 times by water or methanol and then dried in an air oven for 4 hours.

All the reactions were first performed with fresh base-IL medium so as to reach the saturation of product. The yields then were determined in the reuse of the "old" medium.

Methods

Determination of molar mass was performed on a matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) Autoflex III mass spectrometer (Bruker) in linear, positive ion mode with α-cyano-4-hydroxycinnamic acid as matrix. Samples for the mass spectrometry were prepared by dissolving the product (0.10 mg) in DMAc (5.0 mL) at 40°C and then adding 100 μL of this solution to a water/acetonitrile mixture (50:50, 900 μL). The resulting sample was filtered through a 0.02 μm PTFE membrane and injected at a flow rate of 5 μL/min.

Fourier transform infrared (FT-IR) spectra were measured by using a Vertex 70 FT-IR spectrometer (Bruker).

Gel permeation chromatographic (GPC) analysis was performed on an Agilent PL GPC 220 instrument equipped with a Waters 2414 detector and 2 PolarGel-M 10μm columns. All GPC analyses were performed using a DMF solution at a flow rate of 1.0 mL/min at 60 °C and calibrated with polystyrene standards. Samples for GPC analysis were prepared by dissolving the product (0.1 mg) in DMAc with 0.1% LiBr (5.0 mL) at 40°C and filtered through a 0.02 μm PTFE membrane prior to injection.

Tg was measured by using a DSC instrument (Pyris 6, Perkin Elmer). Sample weighed 10.0 mg and the analysis was carried out at a 10 °C/min heating rate under nitrogen purge (25 mL/min). Temperature and heat flow were calibrated using indium and zinc standards.

A TGA instrument (Pyris 6, Perkin Elmer) was used to evaluate the thermal stability of the polyimides. The analysis was carried out at a 10 °C/min heating rate under nitrogen purge (25 mL/min). The weight loss signal was detected as a function of time and temperature.

Table S2

Entry	IL	Base (mol%)	T (°C)	M_n (kDa)	M_w/M_n	Yield[a]/Time
S1	$[C_2mim][OAc]$	-	r.t.	14.2	1.46	Fig. S4
S2	$[C_4mim][OAc]$	-	r.t.	12.5	1.61	Fig. S4
S3	$[C_4mim][PF_6]$	-	r.t.	-	-	0
S4	$[C_4mim][BF_4]$	-	r.t.	-	-	0
S5	$[C_2mim][Et_2PO_4]$	-	r.t.	-	-	0
S6	$[Cho][C_2H_5CO_2]$	-	r.t.	-	-	0
S7	$[C_2mim][OAc]$	-	80	34.1	2.42	Fig. S5
S8	$[C_4mim][OAc]$	-	80	32.4	2.24	Fig. S5
S9	$[C_4mim][PF_6]$	-	80	5.7	2.09	Fig. S5
S10	$[C_4mim][BF_4]$	-	80	11.4	2.71	Fig. S5
S11	$[C_2mim][Et_2PO_4]$	-	80	16.1	2.23	Fig. S5
S12	$[Cho][C_2H_5CO_2]$		80	-	-	0
S13	DMAc	DIPEA (3.00)	r.t.	-	-	0
S14	DMAc	DIPEA (6.00)	r.t.	-	-	0
S15	DMAc	DIPEA (7.50)	r.t.	-	-	0
S16	DMAc	Pyridine (3.00)	r.t.	-	-	0
S17	DMAc	Pyridine (6.00)	r.t.	-	-	0
S18	DMAc	Pyridine (7.50)	r.t.	-	-	0
S19	DMAc	KOtBu (3.00)	r.t.	-	-	0
S20	DMAc	KOtBu (6.00)	r.t.	-	-	0
S21	DMAc	KOtBu (7.50)	r.t.	-	-	0
S22	DMAc	DABCO (3.00)	r.t.	-	-	0

S23	DMAc	DABCO (6.00)	r.t.	-	-	0
S24	DMAc	DABCO (7.50)	r.t.	-	-	0
S11	[C_2mim][OAc]	DIPEA (0.15)	r.t.	-	-	0
S12	[C_2mim][OAc]	DIPEA (0.75)	r.t.	14.5	1.60	Fig. S6
S13	[C_2mim][OAc]	DIPEA (1.50)	r.t.	15.4	1.52	Fig. S6
S14	[C_2mim][OAc]	DIPEA (3.00)	r.t.	18.7	1.55	Fig. S6
S15	[C_2mim][OAc]	DIPEA (4.50)	r.t.	32.6	1.70	Fig. S6
S16	[C_2mim][OAc]	DIPEA (6.00)	r.t.	30.1	1.61	Fig. S6
S17	[C_2mim][OAc]	DIPEA (7.50)	r.t.	32.4	1.84	Fig. S6
S18	[C_2mim][OAc]	DIPEA (30.00)	r.t.	-[b]	-[b]	-
S19	[C_2mim][OAc]	Pyridine (0.15)	r.t.	-	-	0
S20	[C_2mim][OAc]	Pyridine (0.75)	r.t.	-	-	0
S21	[C_2mim][OAc]	Pyridine (1.50)	r.t.	-	-	0 [b,c]
S22	[C_2mim][OAc]	Pyridine (3.00)	r.t.	-	-	0 [b,c]
S23	[C_2mim][OAc]	Pyridine (4.50)	r.t.	-	-	0 [b,c]
S24	[C_2mim][OAc]	Pyridine (6.00)	r.t.	-	-	0 [b,c]
S25	[C_2mim][OAc]	Pyridine (7.50)	r.t.	-	-	0 [b,c]
S26	[C_2mim][OAc]	Pyridine (30.00)	r.t.	-	-	0 [b,c]
S27	[C_2mim][OAc]	KOtBu (0.15)	r.t.	6.7	1.47	Fig. S7
S28	[C_2mim][OAc]	KOtBu (0.75)	r.t.	21.4	1.71	Fig. S7
S29	[C_2mim][OAc]	KOtBu (1.50)	r.t.	16.1	2.23	Fig. S7
S30	[C_2mim][OAc]	KOtBu (3.00)	r.t.	10.7	2.41	Fig. S7
S31	[C_2mim][OAc]	KOtBu (4.50)	r.t.	5.9	2.12	Fig. S7
S32	[C_2mim][OAc]	KOtBu (6.00)	r.t.	4.4	2.22	Fig. S7
S33	[C_2mim][OAc]	KOtBu (7.50)	r.t.	4.2	2.30	Fig. S7
S34	[C_2mim][OAc]	KOtBu (30.00)	r.t.	-[b]	-[b]	-
S35	[C_2mim][OAc]	DABCO (0.15)	r.t.	-	-	0
S36	[C_2mim][OAc]	DABCO (0.75)	r.t.	-	-	0[b,c]
S37	[C_2mim][OAc]	DABCO (1.50)	r.t.	-	-	0 [b,c]
S38	[C_2mim][OAc]	DABCO (3.00)	r.t.	-	-	0 [b,c]
S39	[C_2mim][OAc]	DABCO (4.50)	r.t.	-	-	0 [b,c]
S40	[C_2mim][OAc]	DABCO (6.00)	r.t.	-	-	0 [b,c]
S41	[C_2mim][OAc]	DABCO (7.50)	r.t.	-	-	0 [b,c]
S42	[C_2mim][OAc]	DABCO (30.00)	r.t.	-	-	0 [b,c]

[a] The isolated yield of product in first reuse of base-IL medium.

[b] The product was swollen or dissolved in base-IL medium.

[c] The IL-base medium darkened immediately.

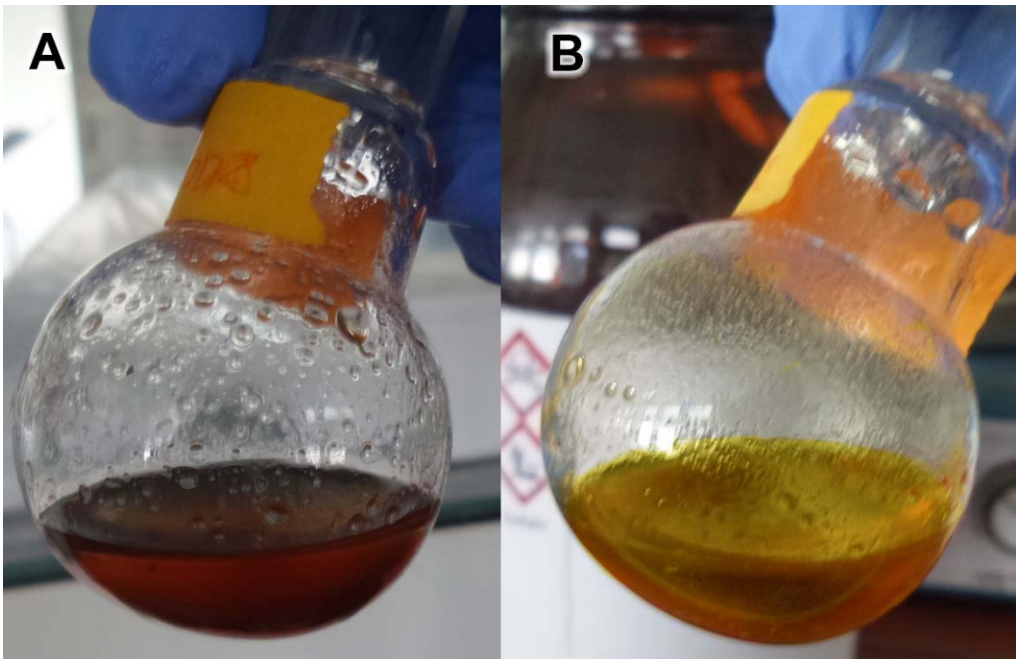


Fig. S1 Observed appearance of the reaction mixtures after 30 minutes, when the PMDA-ODA synthesis reactions were started under the following conditions: (A) in the first use of pyridine (3.00 mol%)-[C_2mim][OAc] medium, and (B) in the first use of DIPEA (3.00 mol%)-[C_2mim][OAc] medium.

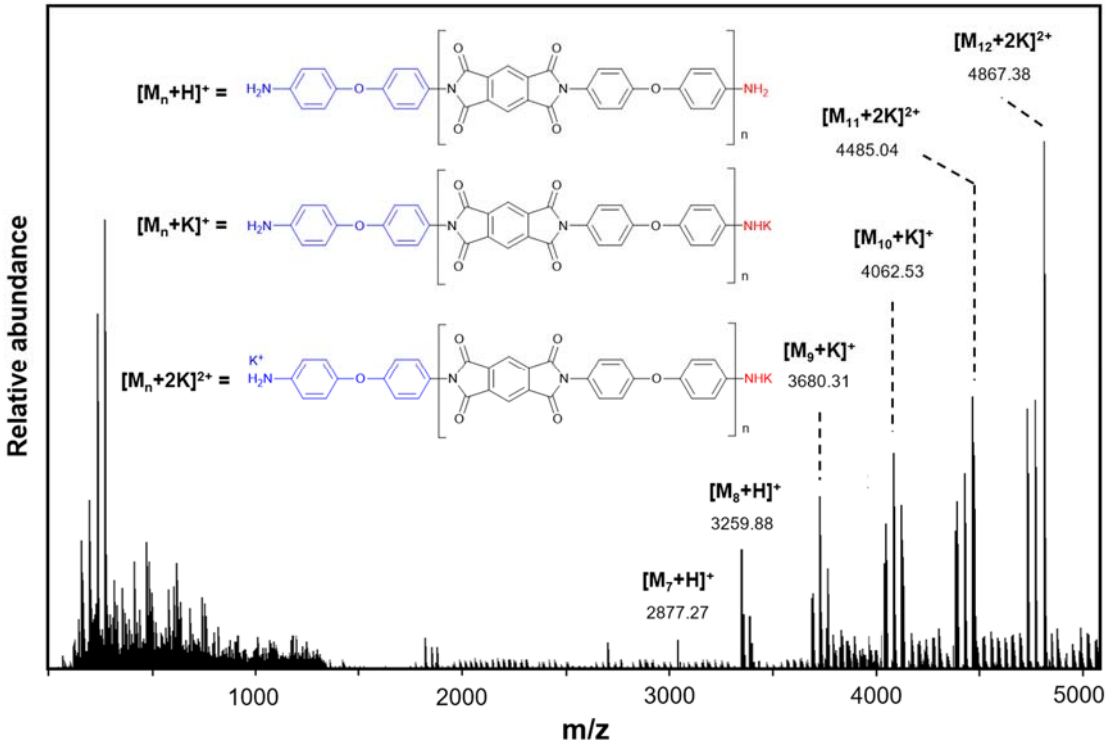


Fig. S2 MALDI-TOF mass spectrum of PMDA-ODA polyimide synthesized from [C_2mim][OAc].

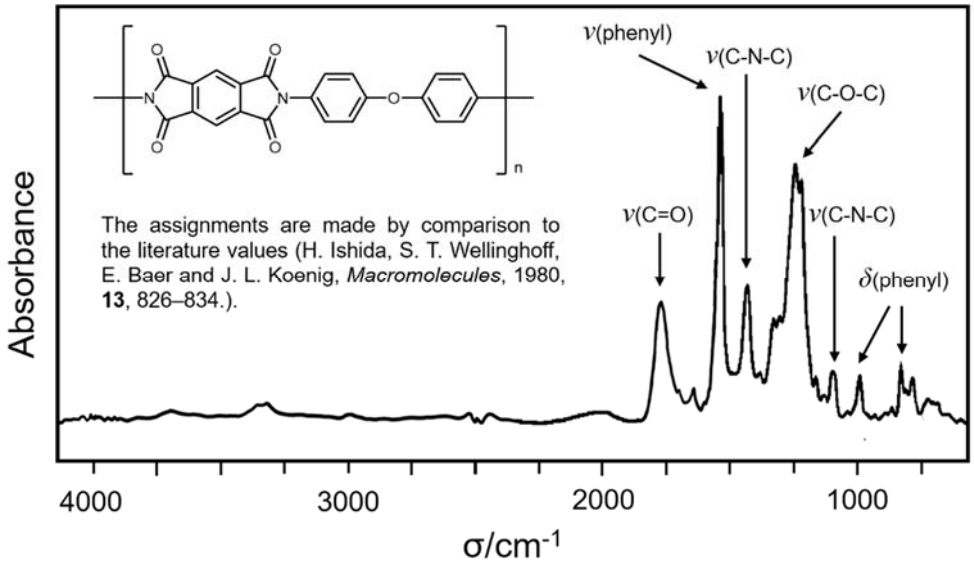


Fig. S3 Infrared spectrum of PMDA-ODA polyimide synthesized in [C2mim][OAc] (film from DMAc).

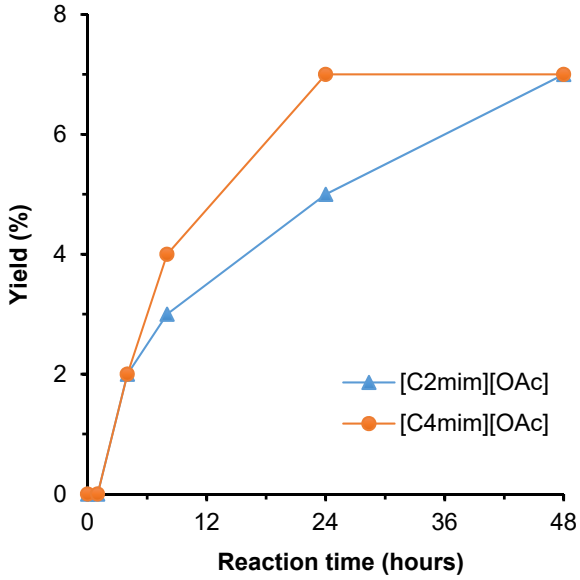


Fig. S4 Yield vs. reaction time profile for the reaction of PMDA-ODA polyimide synthesis in neat ILs at room temperature.

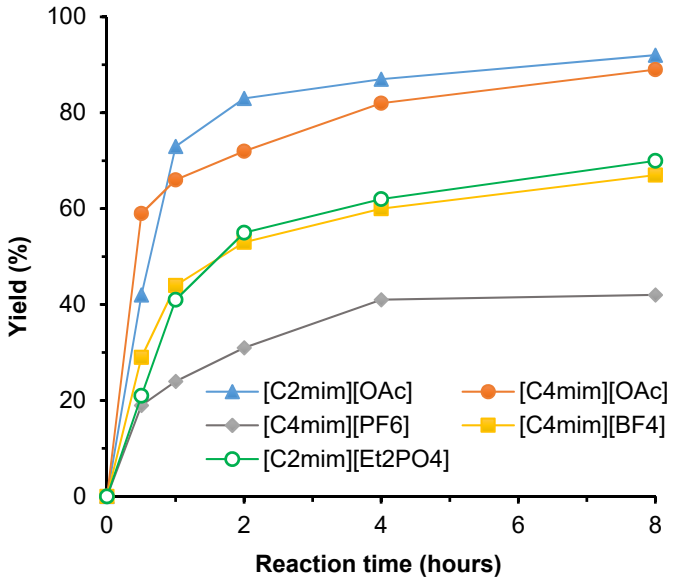


Fig. S5 Yield vs. reaction time profile for the reaction of PMDA-ODA polyimide synthesis in neat ILs at 80°C.

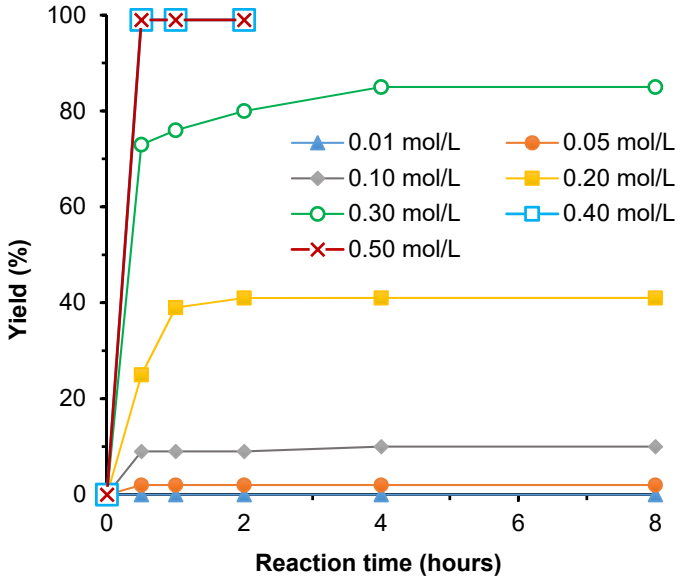


Fig. S6 Yield vs. reaction time profile for the reaction of PMDA-ODA polyimide synthesis in IL containing various concentrations of DIPEA.

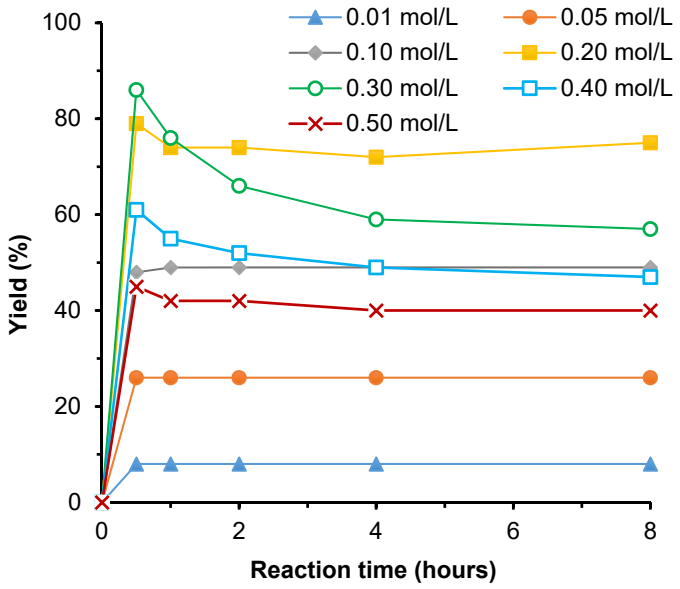


Fig. S7 Yield vs. reaction time profile for the reaction of PMDA-ODA polyimide synthesis in IL containing various concentrations of KOtBu.

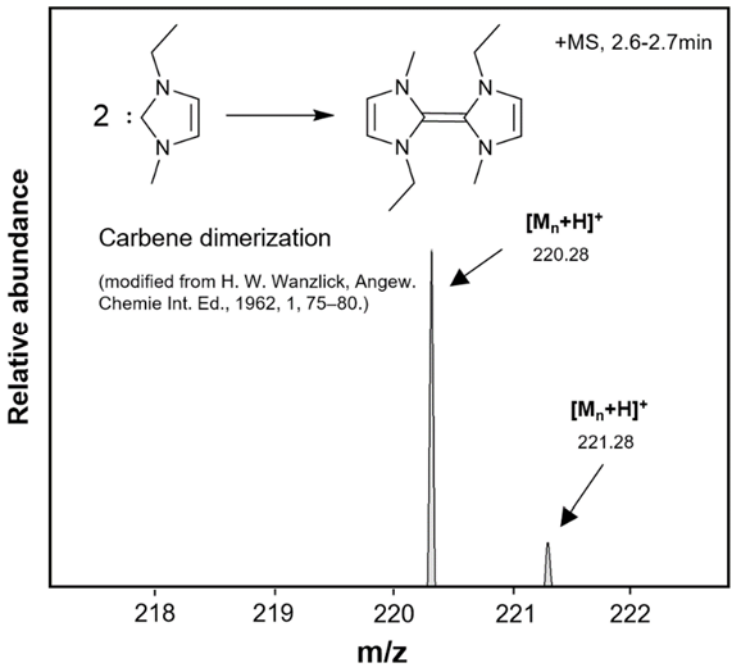
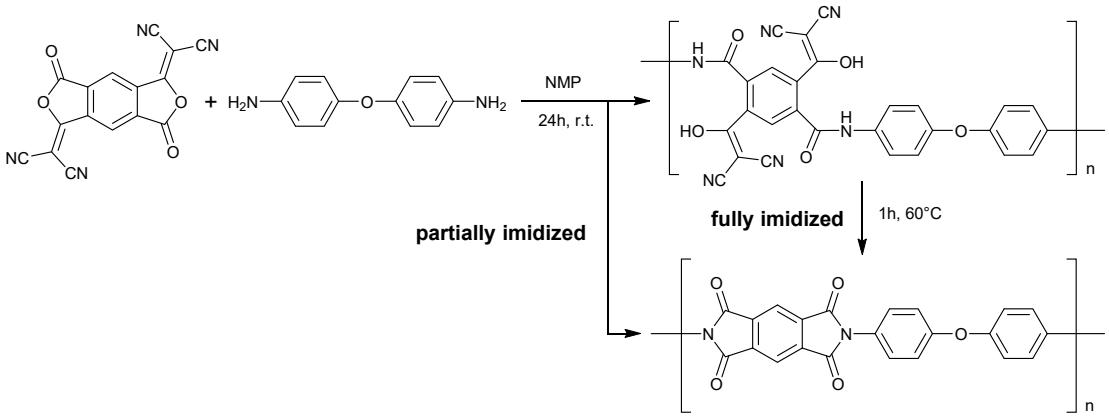


Fig. S8 MALDI-TOF mass spectrum of a separated peak, which appears corresponding to the mass of the carbene dimer.



Scheme S1 Synthesis of PMDA-ODA polyimide by using dicyanomethylidene derivative of PMDA.