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An efficient and mild route to highly fluorinated polyolefins *via* copolymerization of ethylene and 5-perfluoroalkylnorbornenes†

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A series of fluorinated polyolefins have been efficiently synthesized *via* the copolymerization of ethylene with 5-(perfluoro-*n*-alkyl)norbornenes by employing a class of [ONS] titanium catalysts, which possess an open coordination space environment and exhibit excellent tolerance towards fluorine atoms and excellent catalytic activity (up to 1.60×10^6 g (mol h atm)⁻¹). Fluorinated polyolefins with high fluorine contents (up to 44.0 wt%) and high molecular weights ($3.5\text{--}15.9 \times 10^4$ g mol⁻¹) could be obtained under mild conditions. DSC analysis indicated that incorporation of the fluorinated comonomers into polyethylene significantly influences the crystallinity of the polymers (T_m), while it has little influence on the polymer stability.

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Introduction

Transition metal catalysed ethylene copolymerization with various polar comonomers is the focus of considerable research in both academia and industry, since it provides an efficient and effective approach to introduce diverse functional groups into nonpolar hydrocarbon chains and to improve the properties of polyethylene, such as adhesiveness, dyeability, printability, and compatibility.^{1–3} However, achieving copolymerization with both high activity and comonomer incorporation has proved to be quite challenging due to the undesired interactions between the Lewis basic functional groups of the polar comonomers and the electrophilic sites of the active metal catalysts. In recent years, significant progress has been made in this field by designing nickel or palladium complexes.^{3–12} Accordingly, a number of polar monomers including alkyl acrylates, vinyl halides, vinyl ethers, acetonitrile, and vinyl acetates have been identified as suitable

comonomers in the coordination copolymerization with ethylene.

Among the various functionalized polymers, fluorinated polymers play an irreplaceable role due to their remarkable properties,^{13–17} including high chemical stabilities, low surface energies, low dielectric constants and refractive indices.^{18–23} Recently, more attention has been paid to partially fluorinated polymers due to concerns over the safety and processability of perfluorinated polymers^{24–27} and various synthetic strategies have been reported, such as radical copolymerization of ethylene and fluorinated olefins,^{28–31} fluorination of polyolefins,^{32,33} ring opening metathesis polymerization (ROMP) of fluorine-substituted cyclooctenes, and acyclic diene metathesis (ADMET) of fluorine-substituted dienes followed by hydrogenation.^{34,35} In comparison to the above methods, the direct copolymerization of simple olefins with fluoro-substituted olefins by insertion chemistry provides a convenient and long sought-after alternative to synthesize partially fluorinated polymers.^{7,36–41} Since Jordan *et al.* reported the first example of copolymerization of ethylene and vinyl fluoride in 2007,^{37–39} considerable research efforts have been dedicated to this field by using a palladium catalyst.^{40–42} For example, Jordan *et al.* reported the [PO]Pd(Me)(py*) catalysts that incorporated good levels of vinyl fluoride (up to 3.6 mol%) in ethylene polymerization to produce fluorinated HDPE;³⁸ Rieger reported the copolymerization of ethylene and 3,3,3-trifluoropropene in the presence of [PO]Pd(Me)(DMSO) with fluorine contents of up to 15 wt%;⁴⁰ Sen disclosed the copolymerization of ethylene with 4-fluorostyrene (incorporation of 4.5 mol%)⁴¹ and Mecking reported the co- and terpoly-

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merization of ethylene with fluoro acrylate and siloxane acrylate.⁴² However, achieving both high fluorine content and high catalytic copolymerization activity has remained quite challenging up to now. The introduction of the fluorine functionality usually dramatically impairs the catalytic activity because of the strong electron-withdrawing effect of fluorine and β -halogen elimination.^{43–50}

Functional cyclic olefin copolymers (COC), generally prepared *via* the copolymerization of functionalized norbornene type monomers with either ethylene or α -olefin, have attracted considerable attention, due to the multiple advantages of functional polyolefins and COC, such as good adhesiveness, excellent printability, high transparency and low density.^{51–56} To search for a convenient and efficient catalytic system for the synthesis of partially fluorinated cyclic olefin copolymers (COC) *via* insertion chemistry, our group recently carried out the coordination copolymerization of ethylene with 5-(perfluoro-*n*-alkyl)norbornenes. A class of [ONS] titanium complexes, which has previously shown high catalytic efficiency both in the copolymerization of ethylene/norbornene^{57–62} and in the copolymerization of ethylene and polar olefin comonomers,^{63,64} was found to exhibit excellent catalytic activities (up to 1.60×10^6 g (mol h atm)⁻¹). Accordingly, fluoro-substituted copolymers with high fluorine contents (up to 44.0 wt%) and high molecular weights (3.5 – 15.9×10^4 g mol⁻¹) were obtained under mild conditions.

Results and discussion

Synthesis and characterization of fluorinated comonomers and titanium complexes

Three 5-(perfluoro-*n*-alkyl)norbornenes (NBFn) were synthesized *via* the Diels–Alder reaction and purified by vacuum distillation, according to the method reported by Perez *et al.*^{65,66} 5-(Perfluorobutyl)norbornene (NBF4), 5-(perfluoro-

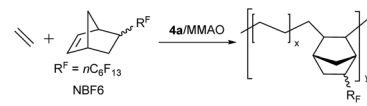
hexyl)norbornene (NBF6) and 5-(perfluorooctyl)norbornene (NBF8) were obtained in 70%, 83%, and 81% yield, respectively.

Complexes **4a–4d** were synthesized, as described previously by our group,^{63,64} in moderate to good yields by treatment of TiCl₄ with ligands. Complexes **4c** and **4d** are new and both were obtained in higher than 80% yields. The molecular structure of **4c** was confirmed by X-ray analysis. The compounds were fully characterized by ¹H, ¹³C, and ¹⁹F NMR spectroscopy and elemental analysis.

The copolymerizations of ethylene with NBF6 catalysed by complex 4a

By employing modified methylaluminoxane (MMAO) as a co-catalyst, we first investigated the copolymerization of ethylene with NBF6 in the presence of complex **4a** that previously showed excellent activity in ethylene homopolymerization⁵⁷ and ethylene/norbornene copolymerization.^{57–62} To our delight, with a MMAO/**4a** (Al/Ti) ratio of 1000 and a NBF6 concentration of 0.075 M in feed, the copolymerization with a NBF6 incorporation of 1.0 mol% and an activity of 0.34×10^6 g (mol h atm)⁻¹ was achieved (Table 1, entry 2). Increasing the Al/Ti ratio from 1000 to 3000 greatly improved both the activity (1.24×10^6 g (mol h atm)⁻¹) and the comonomer incorporation (1.8 mol%) (entry 2 vs. 3, Table 1), which is in line with our previous observation.⁵⁹ The incorporation is closely related to the concentration of the comonomer; on increasing the concentration of NBF6 to 0.38 M, the incorporation of the fluorinated comonomer was enhanced to 4.3 mol%, and the fluorine content reached up to 23.7 wt% (entry 5), while the catalytic activity was maintained at a relatively high level (0.68×10^6 g (mol h atm)⁻¹). In addition, the molecular weights of all the fluorinated copolymers were high (3.46 – 15.5×10^4 g mol⁻¹) and consistent with the increase of the comonomer incorporation (entries 3–5 Table 1), indicating a good tolerance of the catalytic system towards the fluorinated monomers.

Table 1 The copolymerization of ethylene and NBF6 in the presence of **4a**/MMAO^a



Entry	NBF6 [M]	T/°C	Al/Ti	Yield/g	Activity ^b	M _w ^{c,d}	PDI ^c	Incorp. ^e [mol%]	F content ^e [wt%]	T _m ^f [°C]	ΔH _f ^f [J g ⁻¹]	T _g ^f [°C]	T _d ^g
1	0	30	1000	0.758	0.91	8.33	3.35	—	—	133	261.90	ND	449
2	0.075	30	1000	0.283	0.34	15.5	3.11	1.0	7.4	117	167.30	-7.7	446
3	0.075	30	3000	1.033	1.24	6.53	2.74	1.8	12.7	114	113.60	-7.2	443
4	0.150	30	3000	1.137	1.36	8.84	3.04	2.5	16.4	107	86.44	-7.1	442
5	0.380	30	3000	0.567	0.68	14.4	3.22	4.3	23.7	95	43.30	-7.2	448
6	0.075	50	3000	0.400	0.48	3.46	2.88	1.9	13.1	117	129.30	-7.2	444
7	0.380	50	3000	0.283	0.34	5.40	3.49	4.7	25.0	95	41.27	-7.2	445
8	0.075	0	3000	1.083	1.30	9.31	4.97	0.77	6.1	116	122.8	-7.2	—
9	0.075	80	3000	Trace	—	—	—	—	—	—	—	—	—

^a Conditions: Cat. **4a** 5.0 μmol, toluene as the solvent, total volume 50 mL, 10 min, ethylene: 1 atm, MMAO 7.5 mL (2.0 M in heptane). ^b 10^6 g (mol h atm)⁻¹. ^c Determined by GPC in 1,2,4-trichlorobenzene at 145 °C. ^d 10^4 g mol⁻¹. ^e Determined by elemental analysis. ^f Determined by DSC. ^g Determined by TGA at 5% weight loss.

Subsequently, we investigated the effect of temperature by conducting the copolymerization of ethylene with NBF6 at different temperatures. It can be found that both the activity and the NBF6 content at 0 °C are comparable to those achieved at 30 °C, although a slight improvement in molecular weight at 30 °C was observed (entry 3 vs. 8 in Table 1). With the increasing temperature to 50 °C, both the catalytic activity and the molecular weight of the copolymers declined, whereas the NBF6 incorporation increased to 1.9 mol% (entry 6 in Table 1). At 80 °C, no polymer could be isolated.

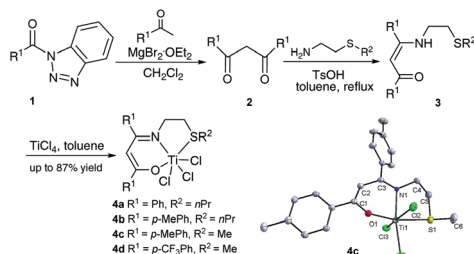
The effect of catalyst on the copolymerizations of ethylene with NBF6

The effect of different titanium complexes (Scheme 1) on the copolymerization was investigated at two concentrations of NBF6 (0.15 M and 0.38 M) respectively. As shown in Table 2, all the substituents (R^1 , R^2 and R^3) on the complexes obviously influenced the copolymerization activity and the comonomer incorporation, and both electronic and steric effects of the catalysts were observed. Compared with complex **4a**, complex **4b** bearing a methyl group at the *para*-position of the aryl group achieved comparable comonomer incorporations but higher activities (entries 1–2 vs. entries 3–4). Replacing the *n*-propyl

group by the methyl group on the sulfur donor usually generates a more open space around the central metal and results in improved copolymerization activity. With complex **4c** as a precatalyst, the copolymerization was achieved with comparative comonomer incorporations and enhanced activities (entries 3–4 vs. entries 5–6). However, compared with the precatalyst **4c**, the introduction of the electro-withdrawing $-\text{CF}_3$ group at the *para*-position of the aryl group, as complex **4d**, resulted in relatively lower activities (entries 7–8 vs. entries 5–6). Besides, compared with the copolymerization of ethylene with norbornene (NBE) at a comparable comonomer incorporation, the experiments using 5-perfluoroalkylnorbornenes as comonomers resulted in lower activities, but much higher molecular weights. This indicated the good tolerance of catalysts towards fluorine atoms (entry 9 vs. entries 4 and 6 in Table 2).

The copolymerizations of ethylene with 5-(perfluoro-*n*-alkyl)norbornenes

Subsequently, we investigated the copolymerizations of ethylene with various 5-(perfluoro-*n*-alkyl)norbornenes, employing complex **4c** under the optimized conditions (with the Al/Ti ratio of 3000 and at 30 °C) (Table 3). Two initial concentrations in feed (0.38 M and 0.75 M) were used for all the three comonomers, namely NBF4, NBF6, and NBF8. As shown in Table 3, all the copolymerizations were achieved with high activities ($0.05\text{--}1.30 \times 10^6 \text{ g (mol h atm)}^{-1}$), high molecular weights (up to $15.9 \times 10^4 \text{ g mol}^{-1}$), and good comonomer incorporations (up to 15.8 mol%). And improving the initial NBF6 concentration to 1.50 M afforded the highest (44.0 wt%) fluorine content (entry 7 in Table 3). All the data demonstrated again that the catalytic system has a good tolerance and copolymerization ability towards the fluorinated comonomers. To the best of our knowledge, this is the highest fluorine content in




Scheme 1 Synthesis of [ONS] titanium complexes.

Table 2 The copolymerizations of ethylene and NBF6 in the presence of **4a–4d**/MMAO^a

Entry	NBF6 [M]	Cat.	Yield/g	Activity ^b	$M_w^{c,d}$	PDI ^c	Incorp. ^e [mol%]	F content ^e [wt%]	T_m^f [°C]	ΔH_f^f [J g ⁻¹]	T_g^f [°C]	T_d^g [°C]
1	0.15	4a	1.137	1.36	8.84	3.04	2.5	16.4	107	86.44	-7.1	442
2	0.38	4a	0.567	0.68	14.4	3.22	4.3	23.7	95	43.30	-7.2	448
3	0.15	4b	1.133	1.36	9.74 ^h	2.24 ^h	2.9	18.4	108	84.63	3.1	—
4	0.38	4b	0.958	1.15	9.41	3.03	5.2	26.7	91	45.53	-7.5	445
5	0.15	4c	1.333	1.60	8.24	2.61	3.0	18.6	108	73.94	-7.2	444
6	0.38	4c	1.083	1.30	11.7	2.81	5.3	27.2	89	47.40	-7.1	445
7	0.15	4d	0.908	1.09	10.1	2.73	2.8	17.7	105	86.89	-7.5	448
8	0.38	4d	0.333	0.40	12.9	4.18	4.5	24.6	90	43.39	-7.4	445
9	NBE ⁱ	4a	1.068	1.28	6.08	3.46	5.9	—	130	122.10	—	455
10	NBE ^j	4a	0.386	0.46	4.74	2.48	10.3	—	86	21.43	—	456

^a Conditions: Cat. **4** 5.0 μmol , MMAO/Ti = 3000 (MMAO: 2.0 M in heptane), toluene as the solvent, total volume 50 mL, 30 °C, 10 min, ethylene: 1 atm. ^b $10^6 \text{ g (mol h atm)}^{-1}$. ^c Determined by GPC in 1,2,4-trichlorobenzene at 145 °C. ^d 10^4 g mol^{-1} . ^e Determined by elemental analysis. ^f Determined by DSC. ^g Determined by TGA at 5% weight loss. ^h Calculated only based on the main peak in the GPC spectrum and the small shoulder peak was ignored. ⁱ NBE 2.0 mmol, Cat. **4a** 5.0 μmol , 10 min. ^j NBE 2.0 mmol, Cat. **4a** 5.0 μmol , 10 min, 50 °C.

Table 3 The copolymerizations of ethylene with 5-(perfluoro-*n*-alkyl)norbornenes in the presence of **4c**/MMAO^a


Entry	Comonomer [mol L ⁻¹]	Time/min	Yield/g	Activity ^b	M_w ^{c,d}	PDI ^c	Incorp. ^e [mol%]	F content ^e [wt%]	T_m ^f [°C]	ΔH_f ^f [J g ⁻¹]	T_g ^f [°C]
1	NBF4 (0.38)	10	0.828	0.99	11.1	4.24	5.2	20.7	90	49.81	-3.5
2	NBF4 (0.75)	20	0.133	0.08	8.48	3.92	9.7	29.8	61	11.30	-3.2
3	NBF6 (0.38)	10	1.083	1.30	11.7	2.81	4.9	25.9	89	47.40	-7.1
4	NBF6 (0.75)	20	0.633	0.38	3.53	4.41	8.6	34.8	62	14.61	3.0
5	NBF8 (0.38)	10	0.911	1.09	15.9	4.18	5.6	32.8	89	47.42	3.8
6	NBF8 (0.75)	20	0.374	0.22	11.7 ^g	3.14 ^g	8.2	39.1	72	13.52	6.6
7 ^h	NBF6 (1.50)	30	0.280	0.05	3.70	3.79	15.8	44.0	ND	ND	15.2

^a Conditions: Cat. **4c** 5.0 μmol , MMAO/Ti = 3000 (MMAO: 2.0 M in heptane), toluene as the solvent, total volume 50 mL, 30 °C, ethylene: 1 atm.

^b 10^6 g (mol h atm)⁻¹. ^c Determined by GPC in 1,2,4-trichlorobenzene at 145 °C. ^d 10^4 g mol⁻¹. ^e Determined by elemental analysis. ^f Determined by DSC. ^g Calculated only based on the main peak in the GPC spectrum and the small shoulder peak was ignored. ^h Cat. **4c** 12.5 μmol .

polyolefins obtained *via* coordination copolymerization so far. Meanwhile, the catalytic activity remained at a relatively high level (0.05×10^6 g (mol h atm)⁻¹). The copolymer samples containing F were difficult to be dissolved well. In some cases, a small shoulder peak could be observed in addition to the main signal, and we suppose that it might have formed due to the strong fluorine–hydrogen bonding force and the cohesion between fluorinate polymers during the polymerization.

Copolymer characterization

Initially, NMR analysis was tried to determine the NBF contents, but the spectra were too complicated to provide a NBF content with certainty and satisfactory accuracy, due to the presence of perfluoroalkyl groups and *endo/exo* isomers.⁶⁸ Therefore, elemental analysis⁴⁰ was performed to estimate the fluorine contents and the corresponding NBF incorporations in the copolymers.

The thermodynamic properties of all the copolymers were characterized by DSC. All the DSC data are listed in Tables 1–3. With the increase of comonomer incorporation, the melting temperature (T_m) and fusion heat (ΔH_f) decreased correspondingly, indicating that the introduction of 5-(perfluoro-*n*-alkyl) norbornene units into the polyethylene backbone destroyed the crystallinity of the polymer chains. This is similar to the case of the ethylene/norbornene copolymerization.⁵⁸ Besides, compared with the ethylene/NBE copolymer, the resultant fluorinated copolymers with similar comonomer incorporation exhibit much lower T_m , ΔH_f and T_g (entry 9 *vs.* entries 4 and 6 in Table 2), which might be due to the fact that the flexible perfluoro-*n*-alkyl chain hanging from the norbornene ring damaged the crystallinity of the polymer chains. On the other hand, the similar T_d values for the fluorinated copolymers, polyethylene and ethylene/NBE copolymer indicated that the introduction of fluorine had little influence on the thermal stabilities of the resulting copolymers.

Experimental section

General procedure

All air or moisture sensitive manipulations were carried out under a highly pure nitrogen atmosphere using Schlenk techniques or in a glovebox. ¹H NMR, ¹³C NMR, and DEPT 135 spectra were recorded on a Varian Mercury 300 spectrometer, Varian 400 NMR spectrometer, Agilent Technologies 600 NMR spectrometer, and JEOL 600 NMR spectrometer, respectively. Mass spectra were obtained with an HP5989A spectrometer. Elemental analysis was performed by the Analytical Laboratory of Shanghai Institute of Organic Chemistry (CAS). M_n , M_w , and M_w/M_n values of the polymers were determined with an Agilent Technologies PL-GPC 220 high temperature chromatograph at 145 °C (polystyrene calibration, 1,2,4-trichlorobenzene as a solvent at a flow rate of 1.0 mL min⁻¹). X-ray crystallographic data were collected using a Bruker AXS D8 X-ray diffractometer. Toluene, hexane, and dichloromethane (DCM) were purified using the MB SPS-800 system. The ligands **3c–d** were prepared by treatment of amine with diketones, through the MgBr₂·OEt₂-promoted aldol addition.⁶⁷

General procedure of ethylene/NBFn copolymerization

A flame-dried Schlenk flask was charged with ethylene and placed in an oil bath at a desired temperature. A desired amount of toluene was transferred into the flask and saturated with ethylene. MMAO and the comonomer were injected into the flask in sequence *via* a syringe, and the mixture was stirred for 10 min. The polymerization was started by adding a precursor catalyst solution in toluene with a syringe. After a desired time, the copolymerization was quenched with acidified ethanol, and the resulting solution was poured into acidified ethanol (300 mL, 10 vol% HCl in ethanol). The precipitated copolymer was collected, washed with ethanol, and then dried at 60 °C under vacuum until a constant weight was achieved.

Synthesis of titanium complexes 4c–4d

[3-(2-(Methylthio)ethylimino)-1,3-di-*p*-tolylprop-1-en-1-olate]Ti(IV)Cl₃ (**4c**). To a stirred solution of TiCl₄ (1.5 g, 8.0 mmol) in dry toluene (50 mL) at –78 °C was added a solution of **3c** (2.0 g, 6.1 mmol) in dry toluene (10 mL) dropwise over 20 min. The solution was allowed to warm to room temperature and stirred for 16 h. The solvent was removed under vacuum and the residue was redissolved in dried toluene (100 mL). The solution was concentrated under vacuum to about 20 mL and was then kept at –30 °C overnight. Reddish black crystals were collected and dried under vacuum to give complex **4c** (2.54 g) in 87% yield. ¹H NMR (300 MHz, CDCl₃, δ): 7.71 (d, *J* = 8.1 Hz, 2H, Ar-*H*), 7.33–7.18 (m, 6H, Ar-*H*), 6.35 (s, 1H, =CH), 4.20–4.02 (m, 2H, NCH₂), 3.28–3.19 (m, 1H, SCH₂), 2.77 (s, 3H, SCH₃), 2.69–2.65 (m, 1H, SCH₂), 2.43 (s, 3H, CH₃), 2.39 (s, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃, δ): 171.1, 170.0, 142.9, 140.1, 134.7, 129.9, 129.7, 129.3, 127.2, 125.9, 109.2, 56.8, 38.1, 22.4, 21.7, 21.4. Anal. calcd for C₂₀H₂₂Cl₃NOSTi (478.69): C 50.18, H 4.63, N 2.93; found: C 50.03, H 4.62, N 2.95.

[3-((2-(Methylthio)ethyl)imino)-1,3-bis(4(trifluoromethyl)phenyl)prop-1-en-1-olate]Ti(IV)Cl₃(**4d**). The same procedures as that used for the preparation of **4c**. Yield: 1.5 g (83%). ¹H NMR (300 MHz, CDCl₃, δ): 7.93 (d, *J* = 8.1 Hz, 2H, Ar-*H*), 7.83 (d, *J* = 8.1 Hz, 2H, Ar-*H*), 7.69 (d, *J* = 8.1 Hz, 2H, Ph-*H*), 7.47 (d, *J* = 7.8 Hz, 2H, Ph-*H*), 6.36 (s, 1H, =CH), 4.19–3.95 (m, 2H, NCH₂), 3.32–3.25 (m, 1H, SCH₂), 2.80 (s, 3H, SCH₃), 2.75–2.71 (m, 1H, SCH₂); ¹³C NMR (75 MHz, CDCl₃, δ): 169.2, 168.2, 140.7, 135.2, 133.4 (q, *J* = 32.3 Hz), 132.2 (q, *J* = 33.4 Hz), 127.4, 126.6, 126.3, 125.9 (q, *J* = 4.0 Hz), 123.5 (q, *J* = 270.6 Hz), 123.4 (q, *J* = 271.1 Hz), 109.5, 57.0, 37.9, 22.6; ¹⁹F NMR (282 MHz, CDCl₃, δ): –63.4, –63.5. Anal. calcd for C₂₀H₁₆Cl₃F₆NOSTi (586.63): C 40.95, H 2.75, N 2.39; found: C 41.18, H 2.85, N 2.26.

Conclusions

In summary, a highly efficient direct coordination copolymerization of ethylene and 5-(perfluoro-*n*-alkyl)norbornenes has been realized for the synthesis of highly fluorinated polyolefins for the first time by using a type of [ONS] titanium complex as the catalyst, which possesses an open coordination space environment and exhibits excellent tolerance towards fluorine atoms. Polyolefins with high fluorine contents of up to 44.0 wt% have been achieved with excellent catalytic activities (0.05~1.60 × 10⁶ g/(mol·h·atm)) and high molecular weights (3.5~15.5 × 10⁴ g/mol). Notably, the introduction of fluorine had little influence on the thermal stabilities of the resulting copolymers, which might provide an attractive way to partially fluoro-substituted COC (copolymer of olefin/cyclic olefin) materials.

Conflicts of interest

The authors declare no conflict of interest.

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