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A New Strategy To Access Polymers with Aggregation-Induced Emission Characteristics

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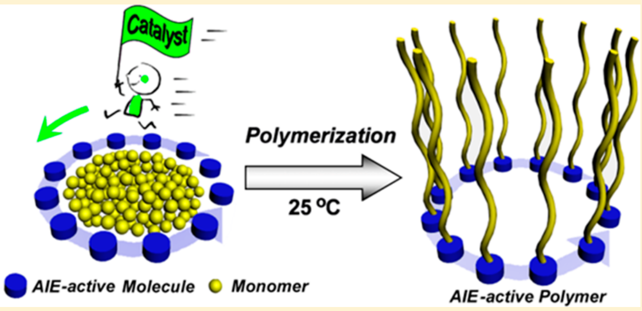
Supporting Information

ABSTRACT: A highly efficient strategy for synthesizing the first biocompatible polyesters with AIE characteristics has been established via immortal ring-opening polymerizations of cyclic esters bearing nonluminophores. In the process, the large excess hydroxyl-modified AIE active compound, acting as the chain transfer agent, attaches to the active rare-earth metal catalyst via the rapid-reversible exchange reaction to initiate the polymerization. Thus, more polyester chains appear to grow from one active metal species, and the AIE fragments are incorporated into the polymer chains at specific sites, *in situ*. The resultant polyesters have linear, block, or star-shaped microstructures mimicking those of the modified AIE compounds. The polymerization solutions can be directly fabricated to large-area thin solid films. The obtained PLA, for instance, emits fluorescence in water/THF mixtures owing to aggregation, the intensity of which is 2850-fold stronger than that in THF solution. This strategy avoids complicated preparation of AIE-active monomers and/or usage of toxic metal reagents for catalyzing the coupling reactions in order to introduce AIE-active fragments, which provides a straightforward approach to access AIE active or other functional polymers from hardly modified monomers.



■ INTRODUCTION

Luminescent materials have gained an upsurge in research interest in the past decades due to their promising applications in electronic and biomedical areas.[1−3] In many cases, however, the luminophores are only highly emissive in dilute solutions, and aggregations often cause partial or even complete quenching of the light emissions (ACQ). To alleviate the ACQ effect in the condensed phase, various chemical, physical, and engineering approaches have been developed,[4] which, sometimes, are accompanied by severe side effects. In contrast, the propeller-like small molecules show "aggregation-induced emission (AIE)" phenomenon coined by Tang and co-workers in 2001, where the aggregation facilitates light-emitting processes of luminogens.[5] Since then, many organic fluorogens have been found to show the AIE effect and many high-tech applications, such as fluorescence sensors, biological probes, immunoassay markers, PAGE visualization agents, and reporters for micelle formation.[6] These low molecular weight luminescent materials with AIE effects have to be fabricated into thin solid films when processing by expensive techniques, such as vacuum sublimation and vapor deposition, prohibiting manufacturing large-area flat-panel devices.

By merit of their good capacity to be facilely fabricated into thin solid films and devices by spin-coating, static casting, and inkjet printing under mild conditions,[7] AIE-active polymers have become the research target. To date, the mostly explored polymers with AIE characteristic are those bearing conjugated double or triple bonds such as polyacetylenes, polyphenylenes, polytriazoles, poly(phenyleneethynylene)s, and poly(phenylenevinylene)s, which are synthesized by polymerization of the monomers modified by the AIE-active luminogens or by attaching the polymers to the predesigned substrates bearing these units via Sonagashira−Hagihara coupling or click reactions.[8] Recently, a few saturated polyolefins (possessing no chromophoric units in their backbones) such as poly(styrene)s, poly(acrylate)s, and poly(acrylamide)s are prepared by anionic or radical polymerizations of the corresponding AIE unit functionalized monomers.[9] Besides these remarkable achievements, development of polymers, in particular, the biodegradable and biocompatible polymers, with *in situ* generated AIE features in more facile manners, obviously, will

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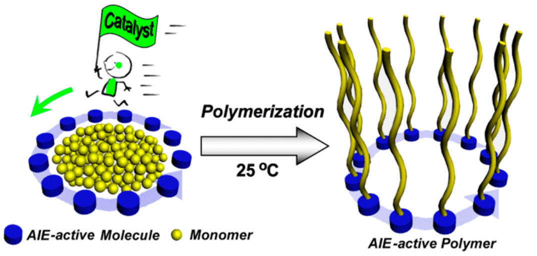
be the next challenging topic: the most promising applications of the AIE-active polymers as the bioprobes of real-time imaging take the furthest advantages of AIE features;[10] the biodegradable polymers are usually arising from hardly functionalized monomers.

Herein, we wish to report a novel and efficient strategy, named "AIE-active molecules mediated chain transfer polymerization", which employs a rare-earth metal catalyst shuttling among the excess AIE-active compounds as the chain transfer agents (CTA) via fast-reversible exchange reaction, to initiate polymerizations. Polymer chains appear to grow from the CTA, thus achieving extremely high catalyst productivity and incorporating the AIE-active units *in situ* into the obtained polymer chains at well-defined positions (Scheme 1). The AIE-active compounds are alcohols in this work; thus, the strategy is suitable for the ring-opening polymerizations (ROP) of cyclic esters. These polyesters are biodegradable and biocompatible materials possessing versatile mechanical properties and low immunogenicity, having been employed as matrixes in pharmaceutical and medical fields as well as imaging and ratiometric sensing applications.[11] Whereas, these polymers are usually hydrophobic and their monomers are hardly functionalized, which make the modification process tedious and complicated. Until now, there are no reports of such AIE-active polyesters.

Scheme 1. Strategy for Synthesizing Polymers with AIE Characteristics

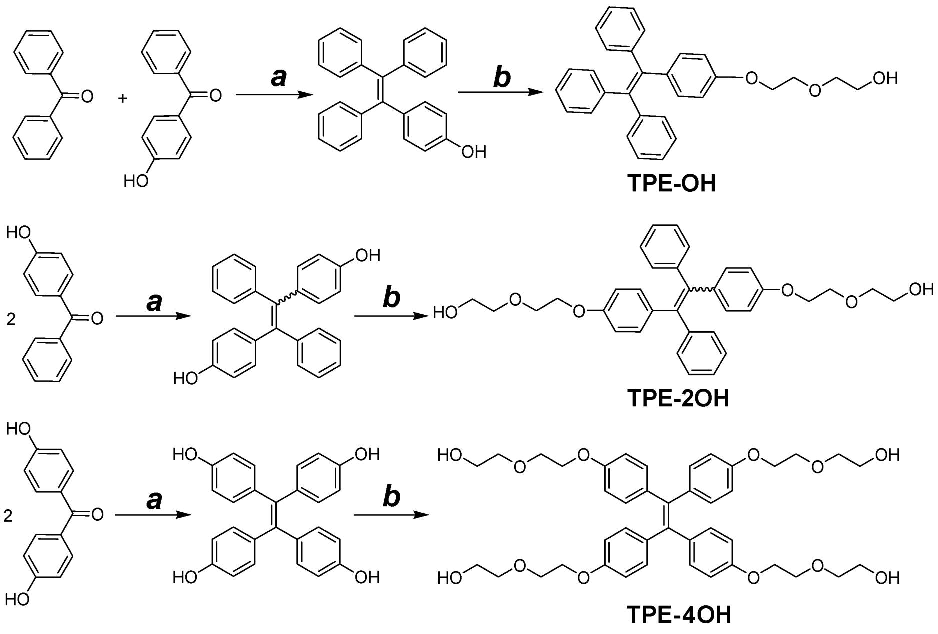


RESULTS AND DISCUSSION

Synthesis of Catalysts Bearing AIE-Active Moiety. The synthesis of the AIE-active polyesters, if tetraphenylethenes (TPE), a typical propeller-like AIE active moiety, is chosen, involves three steps: (1) preparation of the hydroxyl functionalized TPE-*n*(OH) (*n* = 1, 2, 4); (2) reaction of TPE-*n*(OH) with a rare-earth metal coordination catalyst; (3) TPE-*n*(OH)-mediated living-chain transfer ROP of cyclic esters, alternatively, immortal ROP. Mono-, di-, and tetrahydroxyl-functionalized tetraphenylethenes TPE-OH, TPE-2OH, and TPE-4OH were synthesized following the modified literature procedure[12] (Scheme 2). (Details of preparation and characterization are provided in the Experimental Section.) TPE-OH was employed, for the first time, to react stoichiometrically with *O,N,N,O*-tetradentate Salan lutetium alkyl complex **1**.[13] Metathesis reaction between lutetium alkyl moiety Lu−CH_2SiMe_3 in **1** and the hydroxyl group of TPE-OH generated a TPE-labeled Lu−alkoxide counterpart TPE-O-[Lu], selectively (Scheme 3), as evidenced by NMR monitoring result (Figures 1 and Figure S1). Accordingly, treatment of TPE-2OH and TPE-4OH with 2 and 4 equiv complex **1**, respectively, afforded the alkoxide counterparts TPE-2O-[Lu] and TPE-4O-[Lu] in quantitative yields (the ^1H NMR spectrum of TPE-2O-[Lu] and ^1H NMR, ^{13}C NMR, and ^{13}C DEPT (135°) spectra of TPE-4O-[Lu] are shown in Figures S2−S5).

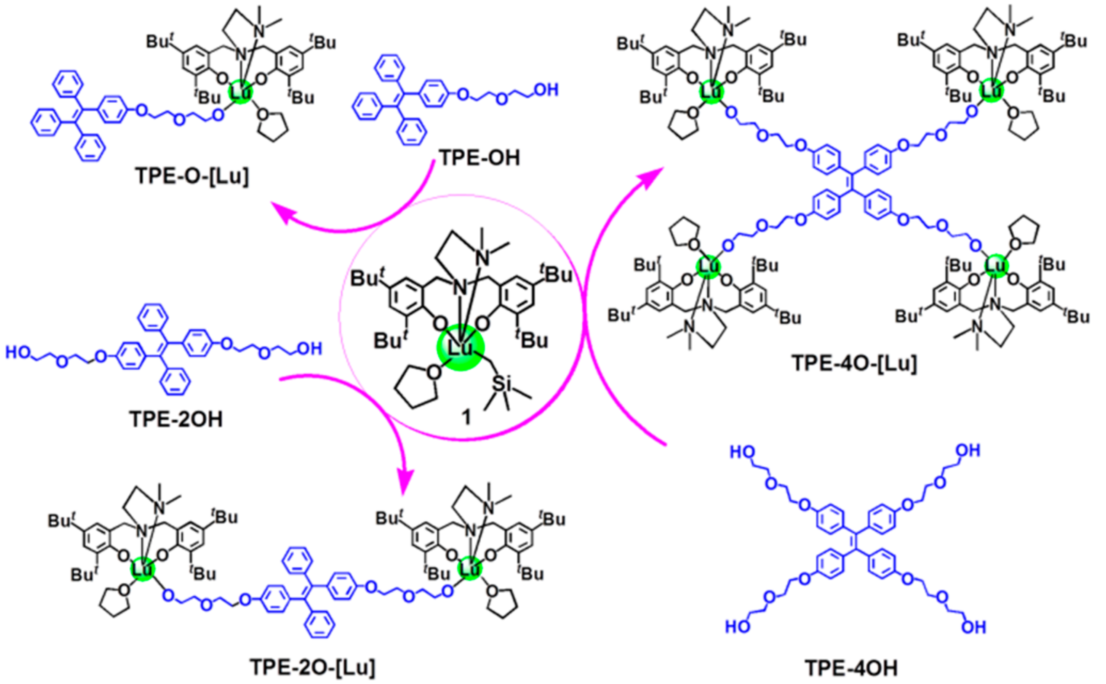
Synthesis of AIE-Active Polymers. To our delight, all the three alkoxide derivatives TPE-O-[Lu], TPE-2O-[Lu], and TPE-4O-[Lu] showed high activity toward the ROP of *rac*-LA in THF at room temperature (Schemes 4 and 5) to transfer 500 equiv of *rac*-LA to polylactide (PLA) within 1 h in high yields (Table 1, entries 1−3). The ^1H NMR spectra of the oligomeric PLA samples indicated that the coordination−insertion of *rac*-LA took place at metal−oxygen bond of each TPE-O-[Lu] unit;

Scheme 2. Synthesis of Hydroxyl-Functionalized TPE[a]



[a] Reagents and conditions: (a) Zn, $TiCl_4$, THF; (b) 2-chloroethoxyethanol, K_2CO_3, KI, DMF.

Scheme 3. Synthesis of TPE-Labelled Lutetium Alkoxide Complexes TPE-O-[Lu], TPE-2O-[Lu], and TPE-4O-[Lu]



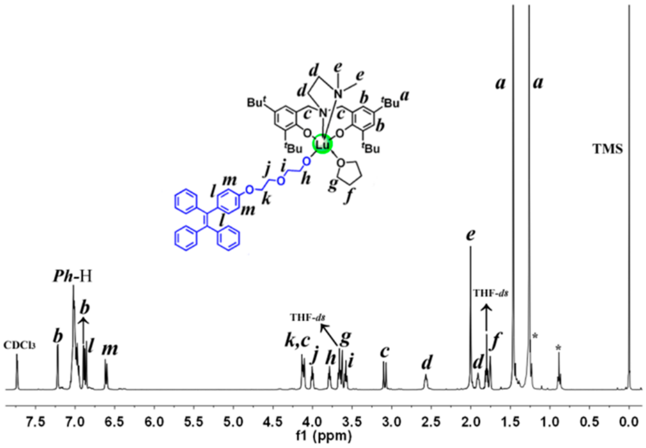


Figure 1. ^{1}H NMR spectrum of TPE-O-[Lu] (400 MHz, THF-d_8 + CDCl$_3$, 25 °C).

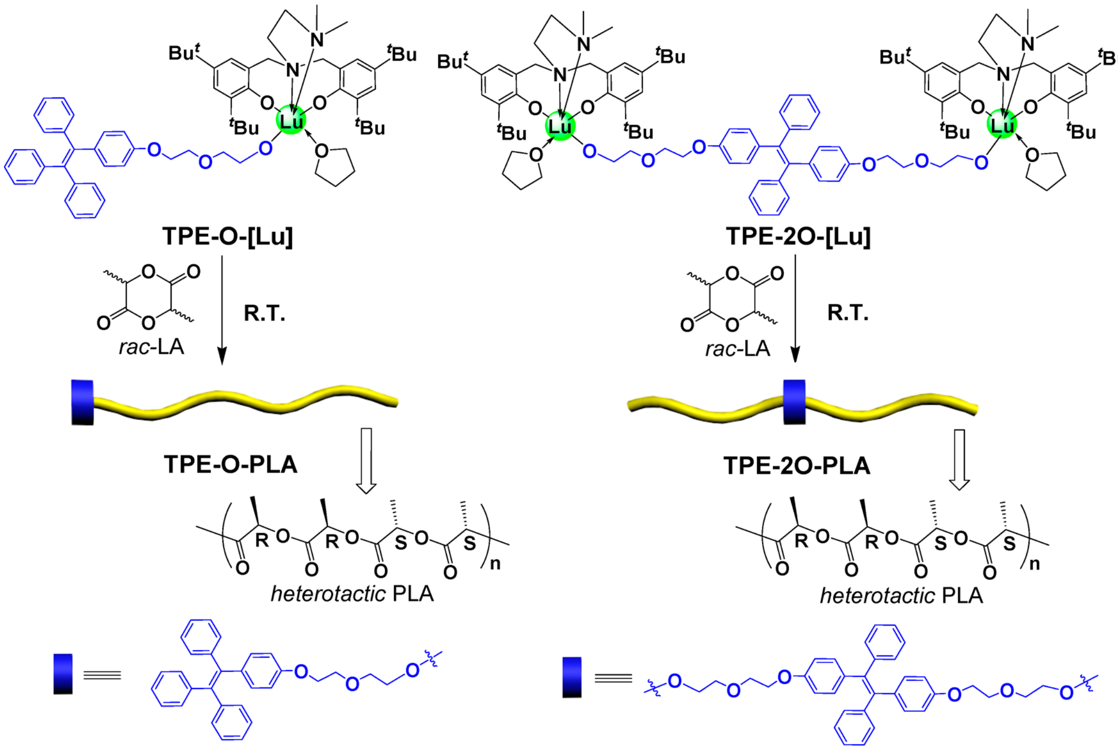
thus, the resultant PLAs were automatically labeled by the TPE moiety at the end (TPE-O-PLA) or the middle of the linear PLAs (TPE-2O-PLA), or the core of the four-armed PLA (TPE-4O-PLA), with respect to the complex employed (Figures 2−4). The resultant PLAs had molecular weights (determined by GPC and $M_{n,GPC}$) very close to those theoretic ones ($M_{n,calcd}$) together with extremely low polydispersity indexes (PDI < 1.06), indicating a living polymerization mode. Moreover, all PLAs possessed very high heterotacticity (P_r = 0.99), which confirmed further that the hydroxyl-modified AIE-active compounds TPE-n(OH) reacted with the lutetium−alkyl moiety exclusively while the Salan ligand remained untouched to govern the selectivity via its cagelike steric environment around metal active center.[13]

The above methodology was extended successfully to other cyclic esters. Under the same polymerization conditions, by using TPE-4O-[Lu] as the initiator, the ROP of CL or the allyl or alkyne functionalized carbonates MAC and MPC went even faster. In the CH$_2$Cl$_2$ medium, TPE-4O-[Lu] could also initiate rapid ROP of *rac*-BBL to give the syndiotactic product (P_r = 0.83) (Scheme 5) (Table 1, runs 4−7). The resultant PBBL, PMAC, and PMPC all have star-shaped microstructures with a AIE-active "core". Noteworthy was that the latter two polycarbonates bear pendant unsaturated C−C double bonds or C−C triple bonds, leaving versatile options for swift postpolymerization modification.

TPE-OH, TPE-2OH, and TPE-4OH Mediated Living Chain Transfer Polymerization. For a living polymerization system, however, one molecule of catalyst leads to the growth of only one macromolecular chain. Thus, the catalyst productivity is low, and a large quantity of the quite expensive catalyst would therefore be required for a relatively small batch of polymer, which is also responsible for the contamination of polymers with high catalyst residue. If the obtained polymers are applied in medical and pharmaceutical (or microelectonic) fields, it always encounters tedious manipulations of catalyst removal and polymer purification to avoid issues revolving around the residual metal traces in the final products. Immortal polymerization (IMP),[14] a special case of coordination chain transfer polymerization (CCTP),[15] where the growing macromolecular chain is able to transfer from the active species to the chain transfer agent (CTA) without occurrence of other chain termination pathways, allowing the growth of several polymer chains per catalyst molecule, is the most efficient manner to carry out a polymerization with the least amount of catalyst. However, the AIE-active TPE-n(OH) have never been employed as the chain transfer agent, whether they can perform the rapid and reversible exchange reaction with the catalyst molecule, the key point of constructing a living immortal polymerization, namely, the catalyst "running fast" among the large amount of TPE-n(OH) to transfer the active moiety to them, is unknown.

Thus, we first attempted the straightforward preparation of the AIE-active initiators by directly mixing "TPE-OH", "TPE-2OH", or "TPE-4OH" with complex **1** ([Lu]/[OH] = 1)

Scheme 4. Synthesis of AIE-Active PLA by Using Salan Lutetium Alkoxide Complexes TPE-O-[Lu] and TPE-2O-[Lu]



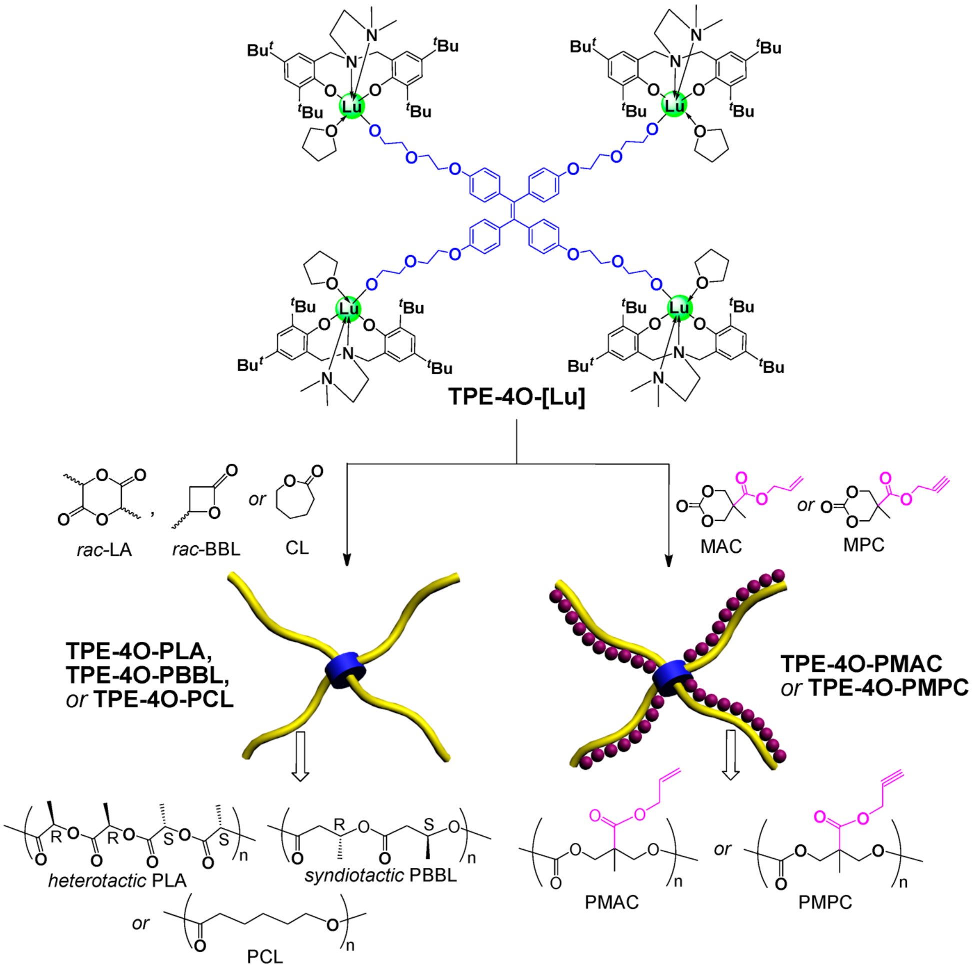
without further work-up process. These *in situ* generated initiators showed the similar performances to the isolated ones, suggesting the formation of the active species was rapid and selective. Enlightented by this result, multiple equivalents TPE-OH were added to the ROP system of *rac*-LA with the [TPE-OH]/[Lu] molar ratio varying from 5:1 to 100:1. Surprisingly to us, the polymerization proceeded smoothly without obvious termination (^{1}H NMR monitoring the reaction of TPE-O-[Lu] with TPE-OH under the molar ratio of 1:3 in the presence of 20 equiv of *rac*-LA in THF-d_8 was shown in Figure S6). The molecular weights (M_n = 0.16 × 10^4–1.45 × 10^4) of the resultant PLAs decreased in inverse proportion with the increase of [TPE-OH], and no broadened molecular weight distribution was observed (PDI = 1.04–1.05), indicative of an immortal polymerization (Table 1, runs 8–11). Moreover, the hetereoselectivity of the precursor **1** (P_r > 0.98) was maintained, suggesting that complex TPE-O-[Lu] was very stable in the presence of large amount of TPE-OH without ligand dissociation from the metal center. TPE-OH behaved as the chain transfer agent to mediate a rapid and reversible exchange reaction with the active species [Lu]-O-TPE (or the simultaneously generated polymeric active species [Lu]-OCHCH$_3$CO-(PLA)-O-TPE). Thus, the resultant PLAs were automatically end-capped with TPE moiety at one end and hydroxyl at the other end, which involved in the polymerization cycle and took the same role as TPE-OH. Therefore, when the polymerization achieved completeness under a [LA]:[Lu]:[OH] ratio of 1000:1:100, 100 PLA chains with TPE-label grew from each active metal center (run 11). When TPE-2OH or TPE-4OH was employed instead of TPE-OH, the ROP of *rac*-LA could also proceed in an immortal fashion to afford linear PLAs with the TPE moiety placed in the middle of the polymer chains or four-armed PLAs with the AIE-active "core" (Scheme 6, Table 1, runs 12–21). So were the cases of *rac*-BBL, CL, MAC, and MPC as the monomers (Table 1, runs 22–26). Obviously, these α-TPE, ω-hydroxyl-functionalized polymers were excellent building blocks for further modification.

Characteristics of the Obtained AIE-Active Biocompatible Polymers. Owing to incorporating TPE moieties, all the obtained polymers were evaluated for their luminescent properties. The AIE-active labeled star polymer TPE-4O-PLA was practically nonluminescent when molecularly dissolved in good solvents, and its photoluminescence (PL) spectrum in dilute THF solution was almost a flat line parallel to the abscissa. Strikingly, as shown in Figure 5a, a strong PL signal was recorded under the same experimental conditions when water was added into the THF solution due to the aggregate formation. The emission intensified gradually with increasing the water fraction f_w in the THF/water mixtures. The enhancement increased rapidly when f_w > 40%. At f_w = 90%, the intensity was more than 2850-fold stronger than that in THF (Figure 5b). The obtained luminogenic materials also displayed good processing property. For instance, the TPE-4O-PLA could be facilely fabricated into large film on a glass substrate by the simple spin-coating. Figure 6a demonstrates the photographs of TPE-4O-PLA-coated glass substrate taken under room light and UV illumination. The coated glass substrate was strongly luminescent under UV illumination. The other isolated polymers also displayed strong luminescence in their solid states under UV illumination (Figure 6b).

CONCLUSION

In summary, we have demonstrated for the first time that polymers with AIE characteristics can be synthesized *in situ* by living chain transfer polymerization. The AIE-active compounds, for instance TPE, are modified with primary hydroxyl groups TPE-*n*(OH), which attach to the active metal centers via metathesis reaction with the coordination catalyst, the Salan-ligated lutetium alkyl complex. Because the exchange reaction between the primary hydroxyl and the lutetium

Scheme 5. Synthesis of Four-Armed, Star-Shaped AIE-Active Biocompatible Polymer by Using Salan Lutetium Alkoxide Complexes TPE-4O-[Lu]



alkoxide is rapid and reversible while the ligand remains untouched, apparently, more polyester macromolecules propagate from one active metal center to achieve an up to 10 000% catalyst efficiency with respect to the amount of TPE-*n*(OH) loaded, and the specific selectivity of the complex is reserved in the cases of *rac*-LA and BBL monomers. Meanwhile, the AIE-active units are incorporated into the polymer chains at well-defined positions relating to the structures of TPE-*n*(OH). The resultant biodegradable polyesters exhibit unique emission properties that were observed in the aggregation states as well as in the solid states. Contrary to the conventional methods, this strategy avoids high catalyst residues, in particular the toxic ones for the coupling reactions, which opens an approach to access biodegradable polymers; those usually arise from hardly modified monomers such as cyclic esters that bear non-luminogens, for their promising real-time imaging and sensor applications.

■ EXPERIMENTAL SECTION

General Procedures. All reactions were carried out under a dry and oxygen-free argon atmosphere by using Schlenk techniques or under a nitrogen atmosphere in an MBraun glovebox. Solvents were purified by an MBraun SPS system. Ligands were synthesized according to modified literature procedures.[1] The phenols and amines were purchased from Aldrich or Fluka. All liquids were dried over 4 Å molecular sieves for a week and distilled before use, and solid materials were used without purification. The synthesis of Salan lutetium complex **1** followed the established method.[13a] D,L-Lactide (Aldrich) was recrystallized three times with dry ethyl acetate. Hydroxyl-functionalized TPEs were synthesized according the literature[12] and dried over anhydrous magnesium sulfate in THF prior to using for polymerization.

Typical Polymerization of *rac*-Lactide in the Presence of Hydroxyl-Functionalized TPE. A typical procedure for polymerization of *rac*-LA in the presence of hydroxyl-functionalized TPEs (TPE-OH, TPE-2OH, or TPE-4OH) was performed in a 25 mL round flask under an N_2 atmosphere. To a vigorously stirred solution of complex **1** in 3 mL of THF was added corresponding hydroxyl-functionalized TPE in 2 mL of THF. After 10 min, *rac*-LA was added quickly. The polymerization took place immediately at room temperature. After a specified polymerization time, an aliquot was withdrawn and quenched quickly with 1.0 mL of $HCl/CH_3OH/CHCl_3$ (0.1/10/60 v/v) solution, and then 1.0 mL of THF was added to obtain a clear solution. Several drops of the quenched solution was taken, removed volatiles, and subjected to monomer conversion determination which was monitored by integration of monomer vs polymer methane or methyl resonances in ^{1}HNMR ($CDCl_3$). The residue solution was quenched by an excess amount of ethanol, filtered, washed with ethanol, and then dried at 40 °C for 24 h *in vacuo* to give polymer product. The molecular weight and the molecular weight distribution of the resulting polymer were determined by GPC. The tacticity of the PLA was calculated according to the methine region homonuclear decoupling ^{1}H NMR spectrum.

Synthesis of Hydroxyl-Functionalized TPEs. *Synthesis of TPE-OH.* This reaction was performed following the procedures described in the literature.[3] A suspension of $TiCl_4$ (0.78 mL, 7.0 mmol) and Zn

Table 1. Immortal Polymerizations of Cyclic Esters with Hydroxyl-Modified TPE Derivatives as the Chain Transfer Agents

run[a]	Mono	CTA	[Lu]/[CTA] /[Mono]	time (min)	conv[b] (%)	$M_{n,calcd} \times 10^{-4}$ [c]	$M_{n,NMR} \times 10^{-4}$ [d]	$M_{n,GPC} \times 10^{-4}$ [e]	PDI[e]	P_r/P_m [f]
1	*rac*-LA	TPE-OH	1/1/500	30	87	6.31		6.40	1.05	0.99/0.01
2	*rac*-LA	TPE-2OH	1/0.5/500	60	94	13.60		14.12	1.03	0.99/0.01
3	*rac*-LA	TPE-4OH	1/0.25/500	60	90	26.02		27.32	1.04	0.99/0.01
4[g]	*rac*-BBL	TPE-4OH	1/0.25/100	10	44	1.59		1.66	1.07	0.83/0.17
5	CL	TPE-4OH	1/0.25/500	1	100	22.90		24.00	1.18	
6	MAC	TPE-4OH	1/0.25/100	10	100	8.08		8.83	1.07	
7	MPC	TPE-4OH	1/0.25/100	10	100	8.00		8.64	1.08	
8	*rac*-LA	TPE-OH	1/5/500	30	87	1.30		1.45	1.04	0.99/0.01
9	*rac*-LA	TPE-OH	1/10/500	60	92	0.71	0.73	0.75	1.04	0.99/0.01
10	*rac*-LA	TPE-OH	1/50/1000	60	73	0.25	0.26	0.27	1.03	0.99/0.01
11	*rac*-LA	TPE-OH	1/100/1000	60	68	0.14	0.15	0.16	1.05	0.98/0.02
12	*rac*-LA	TPE-2OH	1/1/500	30	85	6.18		6.30	1.03	0.99/0.01
13	*rac*-LA	TPE-2OH	1/5/500	30	87	1.31		1.36	1.02	0.98/0.02
14	*rac*-LA	TPE-2OH	1/10/500	30	87	0.68	0.70	0.70	1.03	0.99/0.01
15	*rac*-LA	TPE-2OH	1/50/1000	60	76	0.27	0.26	0.27	1.04	0.98/0.02
16	*rac*-LA	TPE-2OH	1/100/1000	60	55	0.13	0.13	0.14	1.03	0.98/0.02
17	*rac*-LA	TPE-4OH	1/1/500	35	95	6.92		7.12	1.06	0.99/0.01
18	*rac*-LA	TPE-4OH	1/5/500	30	100	1.52		1.64	1.03	0.99/0.01
19	*rac*-LA	TPE-4OH	1/10/500	60	94	0.75	0.76	0.77	1.04	0.99/0.01
20	*rac*-LA	TPE-4OH	1/50/1000	120	73	0.28	0.30	0.30	1.05	0.98/0.02
21	*rac*-LA	TPE-4OH	1/100/1000	120	60	0.16	0.16	0.18	1.05	0.98/0.02
22[g]	*rac*-BBL	TPE-4OH	1/1/300	30	68	1.84		1.77	1.08	0.83/0.17
23[g]	*rac*-BBL	TPE-4OH	1/10/300	30	59	0.73		0.66	1.06	0.82/0.18
24	CL	TPE-4OH	1/5/500	30	100	1.22		1.31	1.04	
25	MAC	TPE-4OH	1/5/500	30	100	2.08		2.16	1.03	
26	MPC	TPE-4OH	1/5/500	30	100	2.06		2.13	1.04	

[a] Polymerizations were performed under N_2 in THF at 25 °C, $[LA]_0 = 0.69$ M. [b] Obtained from ^{1}H NMR analysis. [c] Calculated based on monomer conversion and the assumption that one PLA chain is generated per Lu−O metal species $([Mono]_0/[CTA]_0) \times M_{Mono} \times X$ (X = conv) + M_{CTA}. [d] Determined from ^{1}H NMR spectrum. [e] Determined by GPC in THF using polystyrene standards (the obtained M_n for PLA and PCL were corrected with 0.58 and 0.56, respectively). [f] P_r/P_m of PLA is the probability of racemic/mesomeric linkages between monomer units determined from the methane region of the homonuclear decoupled ^{1}H NMR spectrum, $P_r + P_m = 1$. [g] Polymerizations were performed under N_2 in CH_2Cl_2 at 25 °C, $[BBL]_0 = 1.16$ M, P_r/P_m of PBBL (entries 22 and 23) is the probability of racemic/mesomeric linkages between monomer units determined by $^{13}C\{^1H\}$ NMR spectrum, $P_r + P_m = 1$.

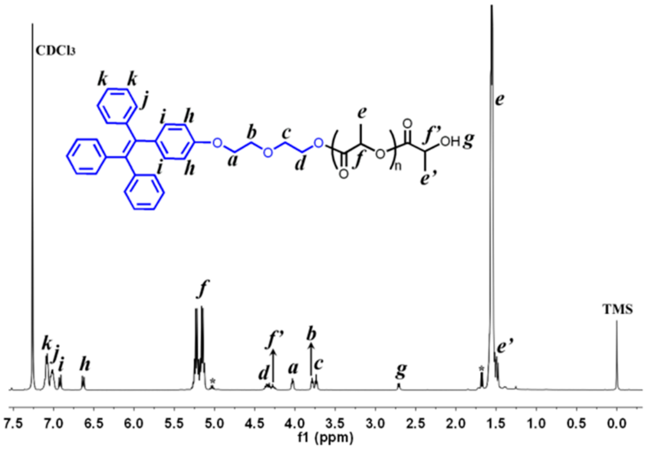


Figure 2. ^{1}H NMR spectrum of oligomeric TPE-O-PLA (400 MHz, $CDCl_3$, 25 °C).

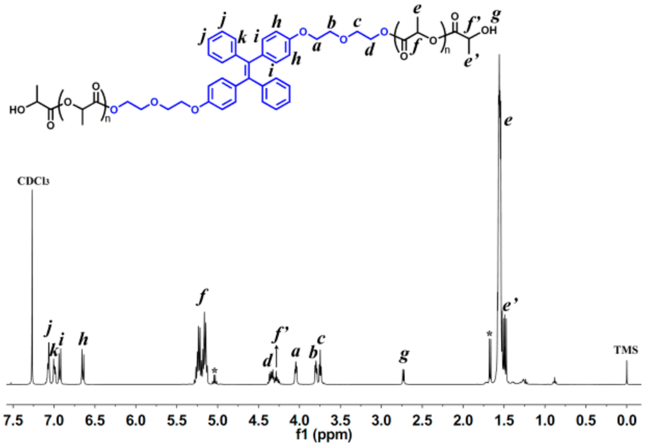


Figure 3. ^{1}H NMR spectrum of oligomeric TPE-2O-PLA (400 MHz, $CDCl_3$, 25 °C).

dust (0.92 g, 14.0 mmol) in 35 mL of dry THF was refluxed under a N_2 atmosphere for 2 h. A solution of 4-hydroxybenzophenone (0.69 g, 3.5 mmol) and benzophenone (0.64 g, 3.5 mmol) in dry THF (15 mL) was added to the suspension of the titanium reagent, and the reaction was allowed to proceed at reflux for 4 h. The reaction mixture was cooled to 25 °C and poured into a 10% aqueous K_2CO_3 solution (50 mL), and after vigorous stirring for 5 min, the dispersed insoluble material was removed by vacuum filtration using a Celite pad. The organic layer was separated, and the aqueous layer was extracted three times with ethyl acetate (25 mL). The combined organic fractions were washed with water and dried over $MgSO_4$. The solvents were removed *in vacuo* to afford 4-(1,2,2-triphenylvinyl)phenol (**M1**). The crude product was purified by a silica gel column using hexane−ethyl acetate (1:1, v/v) as eluent. Compound **M1** was obtained in 65% yield (0.79 g). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ_H = 7.14−6.97 (15H, m, C_6H_5), 6.87 (2H, d, C_6H_4), 6.54 (2H, d, C_6H_4), 4.66 (1H, s, C_6H_4OH)

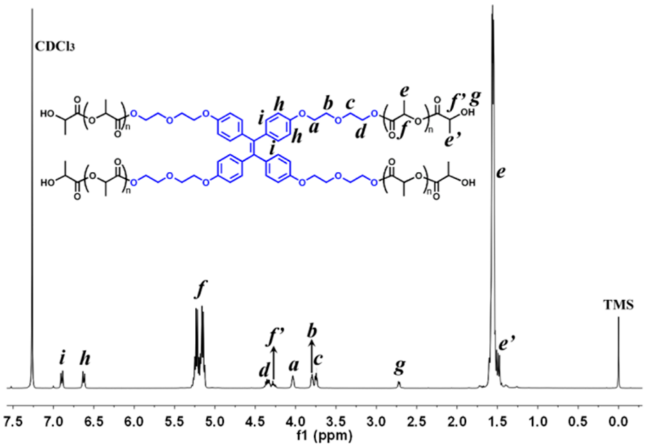


Figure 4. ^1H NMR spectrum of oligomeric TPE-4O-PLA (400 MHz, $CDCl_3$, 25 °C).

A mixture of compound **M1** (0.35 g, 1.00 mmol), 2-chloroethoxyethanol (0.31 g, 2.5 mmol), K_2CO_3 (1.04 g, 7.5 mmol), and potassium iodide (0.16 g, 1.0 mmol) in DMF (25 mL) was stirred at 100 °C for 8 h under a N_2 atmosphere. After removal of solvent, ethyl acetate was added to the mixture. The organic layer was washed with saturated aqueous solutions of $NaHCO_3$, H_2O, and NaCl and dried over anhydrous Na_2SO_4. After filtration and removal of the solvent, the residue was chromatographed over silica gel (ethyl acetate/hexane = 1:4) to give TPE-OH (0.39 g, 90% yield) as a white solid. TPE-OH: ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ_H = 7.14–6.97 (15H, m, C_6H_5), 6.91 (2H, d, C_6H_4), 6.66 (2H, d, C_6H_4), 4.04 (2H, t, $ArOCH_2$), 3.82 (2H, t, $ArOCH_2CH_2$), 3.74 (2H, t, $ArOCH_2CH_2OCH_2CH_2OH$), 3.66 (2H, t, $ArOCH_2CH_2OCH_2CH_2OH$), 2.15 (1H, t, $ArOCH_2CH_2OCH_2CH_2OH$). ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): 157.34 (Ar), 143.67 (Ar), 139.91 (Ar), 136.83 (Ar), 131.07 (Ar), 127.74 (Ar), 126.27 (Ar), 113.55 (Ar), 72.61 (CH_2), 69.49 (CH_2), 66.84 (CH_2), 61.78 (CH_2). MALDI-TOF $[M + 1]^+$: found: 436.2022; calcd: 436.20.

Synthesis of TPE-2OH and TPE-4OH. The synthetic procedures are similar to those of TPE-OH described above. TPE-2OH: White solid; yield 88%. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ_H = 7.14–6.98 (10H, m, C_6H_5), 6.90 (4H, d, C_6H_4), 6.63 (4H, d, C_6H_4), 4.05 (4H, t, $ArOCH_2$), 3.82 (4H, t, $ArOCH_2CH_2$), 3.74 (4H, t, $ArOCH_2CH_2OCH_2CH_2OH$), 3.66 (4H, t, $ArOCH_2CH_2OCH_2CH_2OH$), 2.15 (2H, t, $ArOCH_2CH_2OCH_2CH_2OH$). ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): 157.04 (Ar), 144.17 (Ar), 139.69 (Ar), 136.68 (Ar), 132.54 (Ar), 131.35 (Ar), 127.69 (Ar), 126.24 (Ar), 113.69 (Ar), 72.67 (CH_2), 69.63 (CH_2), 67.18 (CH_2), 61.64 (CH_2). MALDI-TOF $[M+1]^+$: found: 540.2495; calcd: 540.25.

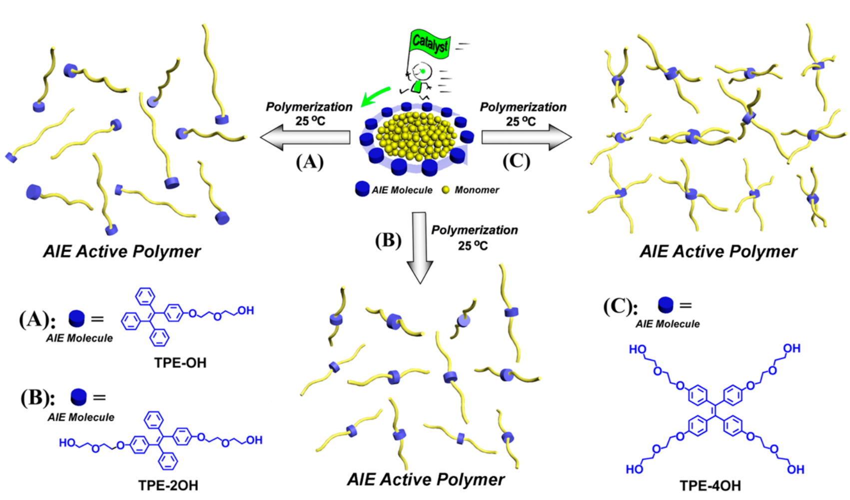
TPE-4OH. White solid, yield 80%. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): 6.91 (8H, d, C_6H_4), 6.65 (8H, d, C_6H_4), 4.07 (8H, t, $ArOCH_2$), 3.83 (8H, t, $ArOCH_2CH_2$), 3.74 (8H, t, $ArOCH_2CH_2OCH_2CH_2OH$), 3.65 (8H, t, $ArOCH_2CH_2OCH_2CH_2OH$), 2.15 (4H, t, $ArOCH_2CH_2OCH_2CH_2OH$). ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): 156.91 (Ar), 138.48 (Ar), 137.07 (Ar), 132.51 (Ar), 113.75 (Ar), 72.63 (CH_2), 69.68 (CH_2), 67.20 (CH_2), 61.69 (CH_2). MALDI-TOF $[M + 1]^+$: found: 748.3448; calcd: 748.35.

Synthesis of Catalysts Bearing AIE-Active Moiety. *Synthesis of Complex TPE-O-[Lu].* To a THF (2.5 mL) solution of complex **1** (0.2 g, 0.2333 mmol) was dropwise added equivalent AIE-OH (0.1018 g, 0.2333 mmol, in 2.5 mL of THF) slowly. After being stirred at 25 °C for 10 min, volatile materials were then removed *in vacuo*, giving complex TPE-O-[Lu] in a quantitative yield (0.28 g). ^1H NMR (400 MHz, THF-d_8 + $CDCl_3$, 25 °C) δ_H 7.22 (2H, d, J_{HH} = 2.5, C_6H_2), 7.09–6.92 (15H, m, C_6H_5), 6.89 (2H, d, J_{HH} = 2.5, C_6H_2), 6.87 (2H, d, J_{HH} = 8.7, C_6H_4), 6.61 (2H, d, J_{HH} = 8.7, C_6H_4), 4.16–4.07 (4H, m, $LuOCH_2$ + $ArCH_2N$), 4.00 (2H, t, J_{HH} = 5.0, $ArOCH_2$), 3.79 (2H, t, J_{HH} = 4.9, $ArOCH_2CH_2O$), 3.63 (4H, s, THF), 3.58 (2H, t, J_{HH} = 5.4, $LuOCH_2CH_2$), 3.09 (2H, d, J_{HH} = 12.3, $ArCH_2N$), 2.57 (2H, t, J_{HH} = 5.5, $N(CH_2)_2N$), 2.00 (6H, s, $N(CH_3)_2$), 1.91 (2 H, t, J_{HH} = 5.5, $N(CH_2)_2N$), 1.76 (4H, s, THF), 1.46 (18H, s, $C(CH_3)_3$), 1.26 (18H, s, $C(CH_3)_3$). Anal. Calcd for $C_{68}H_{89}LuN_2O_6$: C, 67.76%, H, 7.44%, N, 2.32%. Found: C, 67.65%, H, 7.36%, N, 2.23%.

Synthesis of Complex TPE-2O-[Lu]. To a THF (2.5 mL) solution of complex **1** (0.2 g, 0.2333 mmol) was dropwise added 1/2 equiv of AIE-2OH (0.0631 g, 0.1167 mmol, in 2.5 mL of THF) slowly. After being stirred at 25 °C for 10 min, volatile materials were then removed *in vacuo*, giving complex TPE-2O-[Lu] in a quantitative yield (0.24 g). ^1H NMR (400 MHz, THF-d_8 + $CDCl_3$, 25 °C) δ_H 7.22 (4H, d, J_{HH} = 2.5, C_6H_2), 7.06–6.95 (10H, m, C_6H_5), 6.89 (4H, d, J_{HH} = 2.5, C_6H_2), 6.84 (4H, d, J_{HH} = 8.7, C_6H_4), 6.59 (4H, d, J_{HH} = 8.7, C_6H_4), 4.12 (4H, d, J_{HH} = 12.3, $ArCH_2N$), 4.06 (4H, s, $LuOCH_2$) 4.00 (4H, s, $ArOCH_2$), 3.79 (4H, s, $ArOCH_2CH_2O$), 3.64 (8H, s, THF), 3.58 (4H, t, J_{HH} = 5.2, $LuOCH_2CH_2$), 3.08 (4H, d, J_{HH} = 12.3, $ArCH_2N$), 2.56 (4H, t, J_{HH} = 5.5, $N(CH_2)_2N$), 2.00 (12H, s, $N(CH_3)_2$), 1.90 (4H, t, J_{HH} = 5.5, $N(CH_2)_2N$), 1.77 (8H, s, THF), 1.46 (36H, s, $C(CH_3)_3$), 1.26 (36H, s, $C(CH_3)_3$). Anal. Calcd for $C_{110}H_{158}Lu_2N_4O_{12}$: C, 63.57%, H, 7.66%, N, 2.70%. Found: C, 63.49%, H, 7.48%, N, 2.55%.

Synthesis of Complex TPE-4O-[Lu]. To a THF (2.5 mL) solution of complex **1** (0.2 g, 0.2333 mmol) was dropwise added 1/4 equiv of AIE-4OH (0.0436 g, 0.0583 mmol, in 2.5 mL of THF) slowly. After being stirred at 25 °C for 10 min, volatile materials were then removed *in vacuo*, giving complex TPE-4O-[Lu] in a quantitative yield (0.22 g). ^1H NMR (400 MHz, THF-d_8, 25 °C) δ_H 7.22 (2H, d, J_{HH} = 2.5, C_6H_2), 6.90 (2H, d, J_{HH} = 2.5, C_6H_2), 6.86 (2H, d, J_{HH} =8.4, C_6H_4),

Scheme 6. Synthesis of AIE-Active Biocompatible Polymers via a Fast Running Catalyst



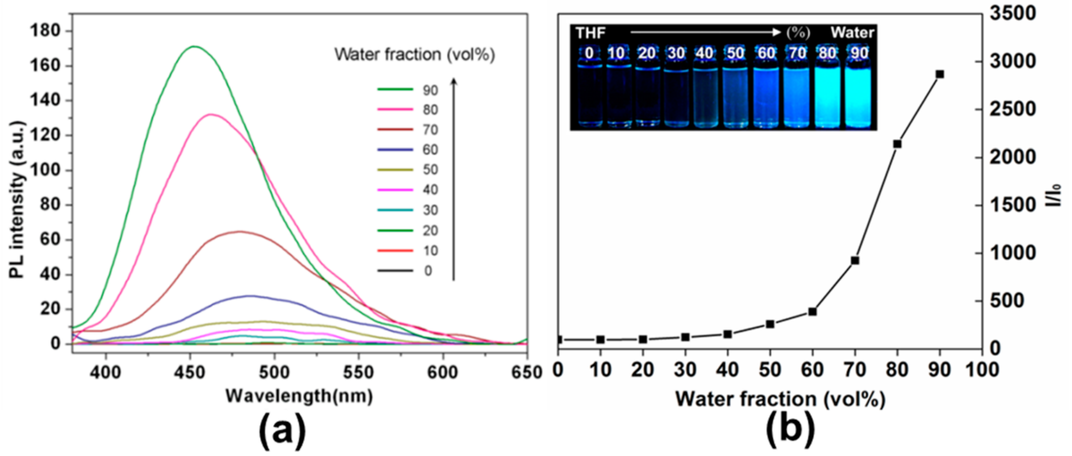


Figure 5. (a) Photoluminescence (PL) spectra of TPE-4O-PLA in THF/water mixtures with different water fractions measured at 25 °C. (b) Plot of I/I_0 versus water fraction in the THF/water mixture (I is PL intensity in THF/water mixtures with different water fractions; I_0 is PL intensity in pure THF solution). Inset: photographs of THF/water mixtures of TPE-4O-PLA with different water fractions taken under UV illumination (TPE-4O-PLA, $M_n = 7.12 \times 10^4$; [TPE-4O-PLA] = 1.0×10^{-5} mol/L).

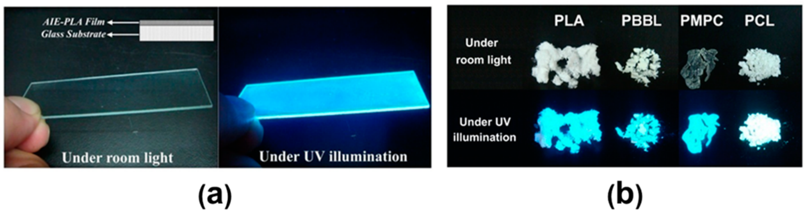


Figure 6. (a) Photographs of AIE-active PLA-coated glass substrate taken under room light and UV illumination. (b) Photographs of star-shaped luminogenic biocompatible polymers under room light and UV illumination.

6.60 (2H, d, J_{HH} = 8.4, C_6H_4), 4.11 (4H, m, $LuOCH_2$ + $ArCH_2N$), 3.97 (2H, t, J_{HH} = 4.7, $ArOCH_2$), 3.75 (2H, t, J_{HH} = 4.7, $ArOCH_2\mathit{CH}_2O$), 3.59−3.52 (6H, m, $LuOCH_2\mathit{CH}_2$ + THF), 3.08 (2H, d, J_{HH} = 12.3, $ArCH_2N$), 2.56 (2H, t, J_{HH} = 5.5, $N(CH_2)_2N$), 2.01 (6H, s, $N(CH_3)_2$), 1.92 (2H, t, J_{HH} = 5.5, $N(CH_2)_2N$), 1.72 (4H, s, THF), 1.47 (18H, s, $C(CH_3)_3$), 1.25 (18H, s, $C(CH_3)_3$). Anal. Calcd for $C_{194}H_{296}Lu_4N_8O_{24}$: C, 60.93%, H, 7.80%, N, 2.93%. Found: C, 60.77%, H, 7.51%, N, 2.76%.

■ ASSOCIATED CONTENT

Supporting Information

^1H−^1H COSY NMR spectrum of TPE-O-[Lu], ^1H NMR spectrum of TPE-2O-[Lu], ^1H NMR, ^{13}C NMR, and ^{13}C NMR (DEPT 135°) spectra of TPE-4O-[Lu], ^1H NMR monitoring of the reaction of TPE-O-[Lu]/TPE-OH (1:3) with 20 equiv of *rac*-LA, UV−vis spectrum of polymer TPE-4O-PLA in $CHCl_3$ solution, MALTI-TOF spectrum of small molecules, ^1H NMR, ^{13}C NMR, and IR spectra of small molecules and polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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