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Introducing SuFEx Click Chemistry into Aliphatic Polycarbonates: A Novel Toolbox/Platform for Post-Modification as Biomaterials

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Experimental procedures

1. Materials

1,5,7-Triazabicyclo[4,4,0]dec-5-ene (TBD, 98.0%, Sigma-Aldrich), 2,2bis(hydroxymethyl)propionic acid (DMPA, 97.0%, TCI), triethylamine (TEA, 99.5%, Aladdin), 1,1'carbonyldiimidazole (CDI, 97.0%, TCI), potassium hydrogen fluoride (KHF₂, 99.0%, TCI), imidazole (98.0%, TCI), 1-metylimidazole (99%, TCI), poly(ethylene glycol) monomethyl ether (mPEG, average molecular weight 2000, TCI), benzoic acid (99.0%, TCI), tert-butyldimethylchlorosilane (TBDMS-Cl, 98.0%, TCl), 6-bromo-1-hexanol (95.0%, TCl), 1-pyrenyl methanol (98.0%, TCl), sodium trifluoroacetate (98.0%, TCI), magnesium sulfate anhydrous (MgSO₂, 99.99%, Aladdin), sodium iodide (NaI, 99.5%, Aladdin), 4-(bromomethyl)benzenesulfonyl chloride (95.0%, Aladdin), poly(ethylene glycol) (PEG, average molecular weight 8000, Aladdin), 2,2,2-trifluoroethanol (TFE, 99.5%, Aladdin), gelatin (type A, BR, Yuanye), lipase (from thermomyces lanuginosus, Sigma-Aldrich), 1H,1H,2H,2H-heptadecafluoro-1-decanol (HDFD, 97.0%, Sigma-Aldrich), 4-(ethyl(2hydroxyethyl)amino)-4-nitroazobenzene (Disperse Red 1, 95%, Sigma-Aldrich), trans-2-[3-(4tertButylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB, 99.0%, Sigma-Aldrich), (4-(1,2,2-triphenylvinyl)phenyl)methanol (TPE-OH, 97%, Bide Pharmatech Ltd.) and other reagents were of analytical grade and used as received. δ -Valerolactone (VL, 98.0%, TCI), anhydrous benzyl alcohol (BnOH, 99.8%, Aladdin), and other reagents employed for polymerization were dried over calcium hydride, vacuum distilled, and then stored over activated 4 Å molecular sieves in an inert atmosphere. Acetonitrile, dichloromethane (DCM), ethyl acetate, ethyl ether, methanol, nhexane, N,N-dimethylformamide (DMF), tetrahydrofuran (THF), toluene, and other solvents

were purchased from Sinopharm Chemical Reagent Co. Ltd. (China) and purified before use according to standard methods. Methanol- d_4 , chloroform-d, and other deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. (Massachusetts, USA). Acetic acid, hydrochloric acid, sodium bicarbonate, sodium chloride, and other aqueous solutions were prepared to the desired concentration.

The gram-negative bacterium *Escherichia coli* (*E. coli*) MG1655 was supplied by the China General Microbiological Culture Collection Center (Beijing, China). LIVE/DEAD BacLight Bacterial Viability Kits were purchased from Invitrogen (Thermo Fisher Scientific). L929 cells (mouse fibroblast cells) were provided by the China Center of Type Culture Collection (Wuhan, China). RPMI 1640 medium (Thermo Fisher Scientific, Inc., Carlsbad, CA), Cell Counting Kit 8 (CCK-8, Beyotime, China), phosphate buffered saline (PBS, Beyotime, China), penicillin (Genview, USA), streptomycin (Solarbio, China), and foetal bovine serum (FBS, Gibco, Invitrogen[™], USA) were used according to the corresponding specifications.

2. Measurements

¹H, ¹³C, and ¹⁹F nuclear magnetic resonance (NMR) spectra were recorded on a Varian Mercury-600 spectrometer (Varian, USA) as well as a Bruker AVANCE III HD-400 spectrometer (Bruker, Switzerland). Chemical shifts (δ) were reported in parts per million (ppm) and were referenced internally relative to tetramethylsilane (TMS, δ 0 ppm) or residual protonated solvent (CD₃OD: δ ¹H 3.31 ppm, CDCl₃: δ ¹H 7.26 ppm) using the residual ¹H and ¹³C solvent resonances. Abbreviations used were s (singlet), d (doublet), t (triplet), q (quartet), b (broad), and m (multiplet).

The number-average molar mass ($M_{n, GPC}$) and polymer dispersity index (*PDI*) values were obtained by gel permeation chromatography (GPC) using a Waters 1515 GPC pump and MZ-Gel SD plus columns with a Waters 2414 refractive index detector (Waters, USA), where specpure DMF was used as the eluent with a flow rate of 1.0 mL/min at 30°C and polystyrene standards were used for calibration. The polymer solution was pressed through a 0.22 µm filter prior to injection.

Fourier transform-infrared (FT-IR) spectra were acquired using a Nicolet 6700 FT-IR spectrometer (Thermo Fisher Scientific Inc., USA). Ultraviolet-visible (UV-vis) absorption spectra and photoluminescence (PL) spectra were measured on a universal microplate reader (Varioskan Flash, Thermo Fisher Scientific Inc., USA). Mass spectra (MS) data of the monomer were obtained using a U3000-MSQ Plus liquid chromatography-mass spectrometer micrOTOF-Q III instrument (Thermo Fisher Scientific (Dionex), Germany). Mass spectral data of polymers were collected using an UltrafleXtreme matrix assisted laser desorption ionization time-of-flight (MALDI-TOF) Autoflex III mass spectrometer equipped with a 1 kHz smart beam-II laser (Bruker, Germany) in reflector mode with positive ion detection. Typical sample preparation for MALDI-TOF MS data acquisition was performed by making stock solutions in the solvent of the matrix (20 mg/mL), polymer analyte (10 mg/mL), and an appropriate cationization agent (10 mg/mL). The stock solutions were mixed in a 10/2/1 ratio (matrix/analyte/cation), deposited onto the MALDI target plate, and allowed to evaporate via the dried droplet method. DCTB was employed as the matrix. Sodium trifluoroacetate was used as the primary cation. MALDI-TOF MS data were calibrated against PMMA calibrants.

Thermal gravimetric analyses (TGA) were performed on a Discovery TGA 55 instrument (TA, USA) under a continuous flow of nitrogen. The thermograms were recorded according to the following cycle: +25 to +600°C at 10°C min⁻¹. Differential scanning calorimetry (DSC) analyses were performed on a Discovery DSC 2500 instrument (TA, USA) apparatus calibrated with indium at a rate of 10°C/min under a continuous flow of nitrogen (25 mL min⁻¹) using aluminum capsules (typically 10 mg of polymer). The thermograms were recorded according to the following cycles: -40 to +200 °C at 10°C/min; +200 to -40°C at 10°C/min. Data of the endothermic curves were recorded from the second scan and analyzed with TA Universal Analysis software (TA Instruments, USA).

Fluorescence images of the stained bacteria were observed by fluorescence microscopy (BX51, Olympus, Japan), and the images were then processed and statistically analysed with Image-Pro Plus software (Media Cybernetics Inc., USA). The microscopic morphology of micelles/vesicles fixed on the copper mesh with carbon supporting film (Beijing Zhongjingkeyi Technology Co., Ltd., China) was taken by a Hitachi HT7700 transmission electron microscope (TEM, Hitachi, Japan). The particle size distribution of micelles/vesicles was analyzed by a dynamic light scattering (DLS) instrument (Zetasizer nano ZS, Malvern Panalytical Co., UK). Electrospun membranes were manufactured by an electrospinning machine (SS-2535H, Beijing Ucalery Industry Technology Development Co., China). The micro-morphology and element analysis of electrospun membrane fibers were measured by a Hitachi SU8010 scanning electron microscope (SEM, Hitachi, Japan) and an Xplore-15 energy dispersive spectrometer (EDS, Oxford Instrument, England). UV light with a wavelength of 365 nm was provided by a ZF-5 portable UV analyzer (Shanghai Troody Analysis Instrument Co. Ltd., China).

3. Experimental Section

3.1. Synthesis of a novel, aliphatic cyclic carbonate monomer: FMC

The general synthetic strategy for FMC is shown in Scheme S1, which requires a three-step procedure, substitution-diol cyclization-substitution. all, i.e., Above 4-(bromomethyl)benzenesulfonyl fluoride¹ and 5-methyl-5-carboxyl-1,3-dioxan-2-one (MCC)² were separately synthesized and purified according to published procedures. Briefly, 4-(bromomethyl)benzenesulfonyl fluoride was produced by the substitution reaction of 4-(bromomethyl)benzenesulfonyl chloride and potassium hydrogen fluoride in an aqueous solution. MCC was synthesized by DMPA following a general procedure for diol cyclization: DMPA (50 mmol, 6.705 g, 1 equiv.), triethylamine (60 mmol, 3.071 g, 1.2 equiv.), and acetonitrile (100 mL) were added to a round bottom flask equipped with a magnetic stirring bar. The reaction mixture was stirred continuously at room temperature until the DMPA was completely dissolved. Afterwards, CDI (87.5 mmol, 14.188 g, 1.75 equiv.) was added, and the mixture was stirred for another 5 min. Excess acetic acid (800 mmol, 45.80 mL, 16 equiv.) was then added to the reaction mixture. Finally, the mixture was loaded into a reflux condenser and stirred at 75°C for approximately 3 hours. At the completion of the condensation, the mixture was cooled to room temperature and then concentrated by a rotary evaporator. The crude residue was dissolved in ethyl acetate and washed with diluted hydrochloric acid. The organic phase was then dried by anhydrous MgSO₄ and removed by rotary evaporation. To remove the residual acetic acid, the resulting residue was fully dissolved in a mixture of ethyl acetate and toluene (50/50, v/v) and concentrated again using a rotary evaporator. Afterwards, the residue was dissolved in a minimal

amount of ethyl acetate, and crystallization was induced by adding hexane. The crystals were then collected by vacuum filtration and washed with additional hexane. ¹H NMR of MCC (400 MHz, CD₃OD) δ = 4.68 (d, *J* = 10.6 Hz, 2H, CH₂(a)), 4.32 (d, *J* = 10.5 Hz, 2H, CH₂(a)), 1.27 (s, 3H, CH₃(b)). (Figure S1, SI).

FMC, the monomer, was then obtained by a substitution reaction of those two compounds. The purified MCC (10 mmol, 1.601 g, 1 equiv.) was dissolved in acetonitrile together with TEA (12.5 mmol, 1.265 g, 1.25 equiv.) and Nal (0.5 mmol, 0.075 g, 0.05 equiv.) and stirred at 40°C. Then, 4-(bromomethyl)benzenesulfonyl fluoride (12 mmol, 3.0 g, 1.2 equiv.) was added to the reaction solution and stirred overnight. The mixture was concentrated by rotary evaporation and dissolved in DCM for extraction. The organic phase was sequentially washed with dilute hydrochloric acid, saturated sodium bicarbonate, and saturated sodium chloride solution. Subsequently, it was dried with MgSO4 and concentrated under reduced pressure. The crude residue was were prepared by dissolution and recrystallization from THF/ethyl ether. The crystals were carefully collected by vacuum filtration and washed with additional anhydrous ethyl ether to obtain the purified product, *i.e.*, FMC (1.64 g, yield ~ 49.4%). The chemical structure was characterized by ¹H (Figure 1a), ¹³C (Figure 1b), and ¹⁹F (Figure S2) NMR, as well as MS (Figure S3) and FT-IR (Figure S4) spectra.

¹H NMR of FMC (600 MHz, CDCl₃) δ = 8.04 (m, 2H, *Aryl-H*(a)), 7.60 (d, *J* = 8.1, 2H, *Aryl-H*(b)), 5.34 (s, 2H, -O*CH*₂(c)-), 4.73 (dt, *J* = 1.5, 11.5, 2H, -(O*CH*₂(d))₂-C-) & 4.25 (dt, *J* = 1.5, 11.5, 2H, -(O*CH*₂(d))₂-C-), 1.35 (s, 3H, -C-*CH*₃(e)); ¹³C NMR (151 MHz, Chloroform-*d*) δ = 170.83 (C-*C*(1)O(O)-CH₂), 147.18 (O=*C*(2)-(OCH₂)₂), 142.94 (Aryl-*C*(3)), 133.26 (Aryl-*C*(4)), 129.01 (Aryl-*C*(5)), 128.71 (Aryl-C(6)), 72.87 ((O-C(7)H₂)₂-C), 66.30 (O-C(8)H₂-benzene), 40.49 ((O-CH₂)₂-C(9)-CH₃), 48.39 (C-C(10)H₃); ¹⁹F NMR (564 MHz, CDCl₃) δ = 66.03 (s).

3.2. Ring-open polymerization catalyzed by TBD

3.2.1 The General Procedure for ROP of FMC

The ROP processes were all carried out under an inert atmosphere with standard Schlenk, vacuum line, and glovebox techniques. As shown in Scheme S2, the initiator (benzyl alcohol, 2.16 mg, 2% mmol, 2% equiv.) and catalyst (TBD, 5.0 mg, catalytic amount) were weighed separately in stoichiometric amounts and then dissolved in THF. FMC (332 mg, 1 mmol, 1 equiv.) was also dissolved in THF. After the reaction system was degassed on a Schlenk line, the monomer solution was then mixed well with the initiator/catalyst solution. The ROP was then reacted at room temperature for 1 h at room temperature in the glovebox. Afterwards, an excess of benzoic acid (8 mg) was added to quench the polymerization by protonating TBD. The mixture was then sufficiently precipitated with cold methanol. After filtered cautiously, the white precipitate was redissolved in additional THF and further reprecipitated in cold methanol for several cycles. Finally, poly(4'-(fluorosulfonyl)benzyl 5-methyl-2-oxo-1,3-dioxane-5-carboxylate), denoted as pFMC for convenience, was vacuum dried at room temperature (135 mg, yield ~ 40%). The chemical structure was characterized by ¹H NMR (Figure 2a), GPC (Figure 2b), MALDI-TOF (Figure S5) and FT-IR (Figure S4) spectra.

¹H NMR (400 MHz, CDCl₃) δ = 7.99 (m, 2H, *Aryl-H*(a)), 7.57 (m, 2H, *Aryl-H*(b)), 5.27 (s, 2H, -OCH₂(c)-), 4.31 (s, 4H, -(OCH₂(d))₂-C-), 1.27 (s, 4H, -C-CH₃(e)); relative to the terminal benzyloxy: (7.35 (s, 5H, C(O)OCH₂C₆H₅(α)), 5.03 (s, 2H, -C(O)OCH₂(β)C₆H₅)).

3.2.2 ROP initiated by different primary alcohols

Based on the excellent initiation effect of benzyl alcohol, other primary alcohols as initiators have also been investigated. Here, 1-pyrenyl methanol (Scheme S3a), which has a fluorescent tracer effect, and polyethylene glycol monomethyl ether (Scheme S3b), which is representative of large molecular alcohols, were selected as examples. Their experimental procedures were based on the *General Procedure for ROP of FMC* section, and the initiator was replaced with equimolar amounts of 1-pyrenyl methanol or polyethylene glycol monomethyl ether. The obtained polymers, *i.e.*, Py-pFMC and mPEG-pFMC were first characterized by ¹H NMR (Figure S6) and GPC, and the comparison of M_n and *PDI* is shown in Table S1.

In addition, photographs and fluorescence emission spectra of ROP initiated by 1-pyrenyl methanol are shown in Figure S6. The fluorescence and photophysical properties of pyrene are attractive and well established.³ Due to the fluorescence of the pyrene group, it is credible that polymers with terminated pyrene groups would also present fluorescent properties.⁴ From the photographs illuminated by UV light at 365 nm (Figure S7a), it was observed that Py-pFMC did not show any significant fluorescence phenomenon compared to PyOH but was similar to pFMC and mPEG-pFMC. However, from the UV absorption spectrum (Figure S7b), Py-pFMC and PyOH show the maximum UV absorption at 320 ~ 350 nm, while pFMC, mPEG-pFMC, and the control group (MeCN the solvent) have no UV absorption at wavelengths greater than 300 nm.

Furthermore, from the fluorescence emission spectrum with an excitation wavelength of 330 nm (Figure S7c), it could be observed that both PyOH and Py-pFMC exhibited the fluorescence emission peak of the pyrene group at 370 \sim 395 nm, while all the other samples had no fluorescent activity under this condition. This result indicated that 1-pyrenylmethanol was still present in the end groups after achieving the initiation of ROP, although the masked pyrene methyl hydrogen was difficult to observe in ¹H NMR.

Thus, it could be demonstrated that the ROP of FMC was well adapted to various hydroxyl initiators.

3.2.3 Expanding the Polycarbonate Platform *via* Copolymerization with a second monomer

Considering the limitations of polycarbonate homopolymer in practical applications, it is usually necessary to introduce a second monomer for copolymerization modification. For example, δ-valerolactone (VL) has often been preferred to modulate degradability and mechanical properties.⁵ Based on this, VL is selected as the second monomer in the study, as shown in Scheme S4. For random copolymerization (simultaneous feeding): FMC (332 mg, 1 mmol, 1 equiv.), VL (100 mg, 1 mmol, 1 equiv.), benzyl alcohol (2.16 mg, 2% mmol, 2% equiv.), and TBD (5.0 mg, catalytic amount) were mixed in THF and ROP was carried out for 1 h at room temperature in the glovebox; an excess of benzoic acid (8 mg) was added to quench the ROP. For block copolymerization (sequential feeding): firstly, FMC (332 mg, 1 mmol, 1 equiv.), benzyl alcohol (2.16 mg, 2% mmol, 2% equiv.), and TBD (5.0 mg, catalytic amount) were mixed in THF and ROP was added to quench the ROP. For block copolymerization (sequential feeding): firstly, FMC (332 mg, 1 mmol, 1 equiv.), benzyl alcohol (2.16 mg, 2% mmol, 2% equiv.), and TBD (5.0 mg, catalytic amount) were mixed in THF and ROP was added to quench the ROP. For block copolymerization (sequential feeding): firstly, FMC (332 mg, 1 mmol, 1 equiv.), benzyl alcohol (2.16 mg, 2% mmol, 2% equiv.), and TBD (5.0 mg, catalytic amount) were mixed in THF and ROP was carried out for 1 h at room temperature in the glovebox; then, VL (100 mg, 1 mmol, 1) equiv.), benzyl alcohol (2.16 mg, 2% mmol, 2% equiv.), and TBD (5.0 mg, catalytic amount) were mixed in THF and ROP was carried out for 1 h at room temperature in the glovebox; then, VL (100 mg, 1 mmol, 1) equiv.), benzyl alcohol (2.16 mg, 2% mmol, 2% equiv.), and TBD (5.0 mg, catalytic amount) were mixed in THF and ROP was carried out for 1 h at room temperature in the glovebox; then, VL (100 mg, 1 mmol, 1) equiv.), benzyl and ROP was carried out for 1 h at room temperature in the glovebox; then VL (100 mg, 1 mmol, 1) equiv.), benzyl and ROP was carried out for 1 h at room tem

1 equiv.) was added into the reaction mixture for another hour; finally, an excess of benzoic acid (8 mg) was added to quench the ROP. The copolymers were precipitated by cold methanol, dried under vacuum, tested, and analyzed.

The ¹H NMR spectra showed that the composition of the copolymers was as expected. As shown in Figure S8, the characteristic peaks of both components, *i.e.*, FMC and VL, appear in ¹H NMR for both p(FMC-*r*-VL) and p(FMC-*b*-VL). Furthermore, the *DP* ratio (x/y) of the two components in the copolymer could be calculated on the basis of the integrated area of the methylene hydrogen (c) from FMC and the methylene hydrogen (1) from VL. For example, in Figure S8, the x/y ratios of p(FMC-*r*-VL) and p(FMC-*b*-VL) are ~ 2.6:1 and 2.2:1, respectively.

These copolymers were also characterized for their thermal properties, *i.e.*, thermogravimetric (TG) analysis and differential scanning calorimetry (DSC). From the TG-DTG thermograms (Figure S9a), it can be observed that p(FMC-r-VL), similar to the homopolymer (pFMC and PVL), exhibits only one thermal weight loss peak; in contrast, p(FMC-b-VL) presents two disparate thermal weight loss peaks. This result indicated the difference in the molecular structure between the random copolymer and block copolymer. In addition, the glass transition temperature (T_g) of the polymers was measured from DSC curves using the transition baseline extrapolation method. The previous analysis revealed that p(FMC-b-VL) contained fewer FMC components than p(FMC-r-VL), and according to the Fox equation, its T_g would be lower, which is in accordance with the results (Figure S9b)

3.2.4 ROP Kinetics of FMC catalyzed by TBD

Similar to the *general procedure for ROP of FMC*, the ROP processes were all carried out under inert atmosphere with an appropriate deuterated reagent as the alternative solvent. Briefly, the initiator (benzyl alcohol, 0.24 mg, 0.5% mmol, 5% equiv.) and catalyst (TBD, 1.0 mg, catalytic amount) were weighed and then dissolved together in chloroform-*d*. FMC (33 mg, 0.1 mmol, 1 equiv.) was also dissolved in chloroform-*d*. After complete degassing of the reaction system, the monomer solution was mixed thoroughly with the initiator/catalyst solution in the glovebox. The ROP reaction was then completed separately and at regular intervals at room temperature. Given the high efficiency of TBD, the timing points were set to 30 s, 1 min, 2 min, 5 min, and 15 min. After reaching the timing points, an excess of benzoic acid (2 mg) was quickly added to quench the polymerization. The reaction solution was tested by ¹H-NMR (Figure S10a, S10b) to monitor the conversion of FMC. As an example, two proton signals on the methylene group attached to benzene can be observed in Figure S10b, which are from the polymers *H*(C) and residual monomers *H*(c), respectively. The percentage of the integrated area of *H*(C) can be calculated to evaluate the conversion rate of FMC, *i.e.*, Equation (1).

$$Conv. = \frac{H(C)}{H(c) + H(C)} \times 100\%$$
 Equation (1)

Here, H(C) represents the integral area of the proton from the benzene-linked methylene in the pFMC; H(c) represents the integral area of the proton from the benzene-linked methylene in the FMC.

Afterwards, it was dried under vacuum and dissolved in DMF for GPC testing (Figure S10c). And the comparison of M_n and *PDI* at the given time is aggregated in Table S2.

In the presence of benzyl alcohol, FMC was polymerized in less than 15 min using TBD as an organocatalyst, and the resulting pFMC showed controllable molecular weight and end-group fidelity from the results above, which was similar to the results of other organocatalytic ROPs of cyclic carbonates but exhibited slightly higher PDI (1.1-1.3) compared to mature ROP (*e.g.,* TMC catalyzed by 1,8-diazabicyclo[5.4.0]undec-7-ene, *i.e.,* DBU).⁵

3.2.5 Chain extension experiments

To further demonstrate the living nature of ROP under experimental conditions, a chain extension experiment was also designed. ROP was initiated with benzyl alcohol and catalyzed by TBD. FMC was added into initiator/catalyst solution with a feeding *DP* of 30 for each cycle. Each cycle was divided into two 30 min periods. At the end of each 30 min of ROP, the test amount of the sample was taken out and the ROP was promptly terminated by adding an excess of benzoic acid. Then the ¹H NMR and GPC tests were performed. Without interval, a new cycle was started with the addition of FMC with appropriate supplementation of TBD. A total of three cycles of chain extension were repeated.

The results are shown in Figure S11. It can be observed that M_n stopped increasing in the second 30 min of each cycle and restarted to increase after the supplemental addition of monomer. Specifically, from the ¹H NMR results (Figure S11b, Table S3), *DP* and $M_{n, NMR}$ increased as the chain extension cycles proceeded. Nevertheless, the characteristic peaks (α and β) of the benzyl group at the end of pFMC became progressively invisible with increasing *DP*, which made it difficult to guarantee the accuracy of the *DP* and $M_{n, NMR}$ calculations. Furthermore, a significant increase in the viscosity of the reaction system occurred with increasing *DP*, which posed a

challenge to purification by simple methanol precipitation. It is also evident in Cycle (3) in Figure S11b, where the polymer contains more impurities. GPC elution curves (Figure S11c), on the other hand, proved that the elution time gradually decreased and $M_{n, GPC}$ progressively increased as the chain extension cycles proceeded. In Table S3, the molecular weight analysis by ¹H NMR and GPC are summarized. It was interesting to note that the results seem to indicate that in the presence of sufficient catalyst, further growth of the intermediate chain can be achieved with the addition of more monomers, which demonstrated the living nature of the ROP.

3.3. The mechanism of TBD-Catalyzed ROP of FMC using DFT methods

A DFT calculation of the ROP of the synthesized monomers catalyzed by TBD was performed to estimate the possible mechanism based on these available mechanistic models (Figure 3). Geometry and frequency calculations for all reported intermediates and transition states were performed with the Gaussian 09 suite of programs⁶ at the B3LYP/6-31G(d,p) level of theory in the gas phase. Harmonic vibrational frequency calculations were performed to verify that no imaginary frequency (for intermediates) or a unique imaginary frequency (for transition states) was obtained. The solvation effects were included using the SMD⁷ continuum solvation model in THF solvent as employed in the experiments. We used the B3LYP density functional with Grimme's empirical dispersion correction (D3) and Becke–Johnson's (BJ) damping schemes. The B3LYP-D3(BJ) functional with the 6-311++G(d,p) basis set was used for solvation single-point energy calculations. Graphical renderings of the optimized geometries were displayed by using the CYL view program.⁸ The specific methods and data are attached to the Supporting Information in Computational Methods.

Previously, it was reported that the possible mechanism of TBD-catalyzed ROP of LLA⁹ and VL¹⁰ was investigated using the density functional theory (DFT) method. Similar to those reported by Goodman,¹⁰ the nucleophilic catalytic mechanism (Mechanism A) and the acid-base catalytic mechanism (Mechanism B) were both investigated carefully (Figure S12). The specific methods and data are attached to the SI.

According to the nucleophilic catalytic mechanism (Mechanism A), **A-Int1** is located after the amidine basic N atom of TBD establishes an H-bond with carbonate. The formation is endergonic by 4.6 kcal/mol relative to the reactants. The calculated free energy barrier to transition state **A-TS1**, relative to the separated reactants, is 22.7 kcal/mol. In **A-TS1**, both C–O dissociation and proton transfer occur simultaneously, yielding acyl intermediate **A-Int2**. The activated BnOH enters the reaction system to form intermediate **A-Int3**, which is an endothermic process with 1.7 kcal/mol. Then, a relatively unstable conformer **A-Int4** is generated. After **A-Int4**, concerted C–O dissociation and proton transfer and elimination occur by overcoming a relatively larger barrier (27.9 kcal/mol) through transition state **A-TS2** to yield the final products.

According to different six-membered conformers in the acid-base catalytic mechanism, Mechanism B, two possible paths are considered. First, intermediated **B-Int1** is reached, in which the carbonyl oxygen is H-bonded to the N–H group of TBD; the O–H group of BnOH is simultaneously H-bonded to the N of TBD. Afterwards, two different ways for concerted C–O formation and proton transfer were located through transition states **B-TS1** and **B-TS3**, respectively, by overcoming activation free energies of 25.5 kcal/mol and 11.2 kcal/mol, and intermediates **B-Int2** and **B-Int4** were generated. After internal rotation, two corresponding

intermediates **B-Int3** and **B-Int5** are also considered with negligible barriers where no transition states are obtained. Finally, similar to that discussed in Mechanism A, concerted C–O dissociation and proton transfer and elimination occur by overcoming a relatively lower barrier of 14.7 kcal/mol (**B-TS2**) and 12.2 kcal/mol (**B-TS4**) to yield the final products. In contrast, a relatively higher Gibbs free barrier of 27.9 kcal/mol (**A-TS2**) is calculated in the mechanism, which is the highest barrier. Clearly, a favorable pathway through **B-TS3** and **B-TS4** is kinetically more favorable than that through **A-TS1** and **B-TS1**, suggesting the acid-base catalytic mechanism of the TBD-catalyzed ROP of FMC.

3.4. Chemical degradation of pFMC in vitro

Dried pFMC (Unless otherwise specified, the pFMCs used below are all of this specification: $M_n \sim 6.5$ kDa, $DP \sim 20$) powders were weighed and immersed in PBS solution (pH 7.4). These solutions were then placed in an ambient shaker incubator at 37°C and shaken at 90 rpm. In another group, the polymers were subjected to the same incubation conditions, and an additional 0.1 wt% lipase was added to the PBS solution. In each group, the solution was changed at a frequency of every 3 days to prevent the accumulation of solute concentration in the solution. After reaching the experimentally preset time interval, the residual polymer was filtered out, rinsed with deionized water, and freeze-dried to a constant weight. The mass of the residue was recorded. Degradation was monitored and evaluated by the mass change (Figure S13) during degradation. The mass change was calculated from Equation (2):

$$Mass change = \frac{wt(0) - wt(n)}{wt(0)} \times 100\%$$
 Equation (2)

Where *wt(0)* is the initial weight of the pFMC before degradation, and *wt(n)* represents the dry weight of residue after each degradation cycle.

3.5. Cytocompatibility of pFMC in vitro

Cytotoxic tests in vitro were performed to investigate cytocompatibility. pFMCs were first dissolved in acetonitrile and flow-cast in PS cell culture 96-well plates, which were denoted as pFMC coatings. Another set of PS well plates was taken as a blank control. Then, both PS well plates and pFMC coatings were sterilized by UV light before processing.

L929 cells (mouse fibroblast cells) were cultured in RPMI 1640 medium supplemented with 10% FBS, 100 U/mL penicillin and 100 μ g/mL streptomycin. Culture media were changed every day. Cells were detached from the cell culture flask by trypsinization, collected by centrifugation at 185 rad/s for 5 min and resuspended in a fresh cell culture medium before experiments. L929 cells were seeded in the cell culture 96-well plates coated with pFMC at a density of 2×104 cells per well and incubated for 24h, 48h, and 72 h. Culture media were changed every day. At the determined times, 200 μ L RPMI 1640 and 20 μ L CCK-8 dye were added to each well, and then the 96-well plate was kept in an incubator at 37°C for 2 h. 100 μ L of the solution was transferred to a new 96-well plate. The absorbance of each solution at 450 nm was recorded by a microplate reader and presented as optical density (*OD*) values. Every treatment was repeated 6 times. As a blank control, the same operation was performed on the PS well plates. The relative cell viability was evaluated by comparing the *OD* values and results were shown in Figure S14.

3.6. PPM of pFMCs for biomedical applications

3.6.1 Synthesis of Silyl Ether-Protected Compounds:

Synthesis Protected Imidazolium of Silvl Ether Ionic Liquid (1-(6-((*tert*butyldimethylsilyl)oxy)hexyl)-3-methyl-1H-imidazol-3-ium bromide, TBDMS-IL): The synthesis of TBDMS-IL was performed with reference to previously published synthetic routes.¹¹ Briefly, 6bromo-1-hexanol (3.0 g, 16.6 mmol), imidazole (3.0 g, 44 mmol), and TBDMS-Cl (3.0 g, 20 mmol) were dissolved in 50 mL of DCM, and the reaction was allowed to stir overnight. The mixture was extracted by ultrapure water and saturated brine sequentially. The organic phase was collected and purified by column chromatography (MeOH/DCM: 1/20, v/v). Then the organic solvent was removed by rotary evaporation. ((6-Bromohexyl)oxy)(tert-butyl)dimethylsilane, the intermediate product, was dried overnight in a vacuum drying oven to yield 4.41 g (~ 89%) of a clarified oily liquid. Methylimidazole (0.9 g, 11 mmol) was added dropwise to the intermediate product (3 g, 10.2 mmol) and stirred overnight at room temperature under a nitrogen atmosphere. The mixture was then washed several times in cold ether. After drying under vacuum, a colorless viscous liquid, TBDMS-IL, was obtained (yield 3.45 g, ~ 90%).

Synthesis of Silyl Ether-Protected Polyethylene Glycol Monomethyl Ether (*tert*-butyl(2methoxy polyethoxy)dimethylsilane, *TBDMS-mPEG*): The synthesis of TBDMS-mPEG was performed with reference to previously published synthetic routes.¹¹ Polyethylene glycol monomethyl ether (mPEG, $M_n \sim 2000$ Da, 3 g, 1.5 mmol), imidazole (0.21 g, 3.1 mmol), and TBDMS-Cl (0.24 g, 1.6 mmol) were dissolved in 10 mL of DCM, and the reaction was allowed to stir overnight. The reaction solution was washed and settled several times by dropping into the refrigerated ether. Then, the precipitate was filtered out and dried under a vacuum. A white powder was obtained in a yield of 2.96 g.

Synthesis of bis-Silyl Ether-Protected Polyethylene Glycol (polyethylene glycol bis(*tert*-butyl dimethylsilane) ether, *bisTBDMS-PEG*): Polyethylene glycol (PEG, $M_n \sim 8000$ Da, 8 g, 1 mmol), imidazole (0.30 g, 4.4 mmol), and TBDMS-Cl (0.33 g, 2.2 mmol) were dissolved in 100 mL of DCM, and the reaction was allowed to stir overnight. The reaction solution was redissolved with DCM. The organic phase was collected by extraction and then concentrated by rotary evaporation. The concentrated solution was washed and settled several times by dropping it into the refrigerated ether. Then, the precipitate was filtered out and dried under a vacuum. A white powder was obtained after drying in a yield of 8.60 g.

Synthesis of Silyl Ether-Protected 1*H*,1*H*,2*H*,2*H*-Heptadecafluoro-1-decanol (*tert*butyl((3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10 heptadecafluorodecyl)oxy)dimethylsilane, *TBDMS*-*HDFD*): The synthesis of TBDMS-HDFD was performed with reference to previously published synthetic routes.¹² 1*H*,1*H*,2*H*,2*H*-Heptadecafluoro-1-decanol (HDFD, 0.93 g, 2 mmol), imidazole (0.33 g, 4.8 mmol), and TBDMS-CI (0.30 g, 2 mmol) were dissolved in 20 mL of DCM, and the reaction was allowed to stir overnight. The mixture was extracted by ultrapure water and saturated brine sequentially, and the organic phase was collected and purified by rapid column chromatography. The organic phase was then dried by adding a sufficient amount of anhydrous MgSO₄, and then the organic solvent was removed by rotary evaporation. The residue was dried overnight in a vacuum drying oven to yield 1.04 g (~ 90%) of clarified oily liquid.

Synthesis of Silyl Ether-Protected Disperse Red 1 (*N*-(2-((*tert*-butyldimethylsilyl)oxy)ethyl)-*N*-ethyl-4-((4-nitrophenyl)diazenyl)aniline, *TBDMS-DR1*): The synthesis of TBDMS-DR1 was performed with reference to previously published synthetic routes.¹¹ Disperse Red 1 (DR1, 1 g, 2.59 mmol), imidazole (0.42 g, 6.22 mmol), and TBDMS-Cl (0.43 g, 2.84 mmol) were dissolved in 20 mL of DCM, and the reaction was allowed to stir overnight. The mixture was extracted by ultrapure water and saturated brine sequentially, and the organic phase was collected. The organic phase was dried by adding a sufficient amount of anhydrous MgSO₄, and then the organic solvent was removed by rotary evaporation. The residue was dried overnight in a vacuum drying oven to yield 1.12 g (~ 82%) of a dark red powder.

Synthesis of Silyl Ether-Protected Tetraphenyl Ethylene (*tert*-butyldimethyl((4-(1,2,2-triphenylvinyl)benzyl)oxy)silane, *TBDMS-TPE*): (4-(1,2,2-triphenylvinyl)phenyl)methanol (TPE-OH, 0.362 g, 1 mmol), imidazole (0.15 g, 2.2 mmol), and TBDMS-Cl (0.18 g, 1.2 mmol) were dissolved in 10 mL of DCM, and the reaction was allowed to stir overnight. The mixture was extracted by ultrapure water and saturated brine sequentially, and the organic phase was dried by adding a sufficient amount of anhydrous MgSO₄ and concentrated by rotary evaporation. The residue was separated by column chromatography (MeOH/DCM: 1/60, v/v) and dried in a vacuum to obtain the final product as a white powder with a yield of 0.46 g in ~ 96%.

3.6.2 PPM of pFMCs via the SuFEx click reaction with silvl ether-protected functional modules (Scheme S5):

Antimicrobial pFMCs: The specific synthetic procedure of antimicrobial pFMCs (Scheme S6a) is as follows: pFMCs (333 mg) were dissolved in 5 mL acetonitrile with thorough stirring to

homogenize the solution, and silvl ether-protected imidazolium-type ionic liquid (TBDMS-IL, 126 mg) and TBD (5 mg) were added with continuous stirring. After reacting for 15 min at room temperature, the solution was drip-precipitated into cold methanol. The precipitates were then repeated three times through a redissolution-precipitation cycle. The precipitate, pFMC-IL, was finally filtered out and dried under vacuum overnight. The chemical structures, $M_{n, GPC}$, and *PDI* were respectively measured by ¹H NMR and GPC (Figure S15).

pFMCs (10mg) and pFMC-IL (15 mg) were dissolved in 200 µL acetonitrile and flow-cast into membranes in PS cell culture 96-well plates, which were recorded as pFMC coatings and pFMC-IL coatings, respectively. At the same time, an equal amount of acetonitrile was dropped into PS cell culture 96-well plates, and the organic solvent was completely evaporated to make a blank group, which was recorded as PS well plates. *Escherichia coli (E. coli)* MG1655 was selected as a model bacterium to evaluate the antibacterial properties and cultured as reported¹³. Briefly, the sample surfaces were carefully sterilized with 75% alcohol, rinsed with PBS 3 times, and then incubated with 100 µL of *E. coli* suspension (~ 1×10^7 CFU/mL) at 37°C for 3 h. After rinsing 3 times with PBS, LIVE/DEAD BacLight Bacterial Viability Kits were used to evaluate the antibacterial properties. The surfaces were gently and adequately rinsed with PBS and sterile water before fluorescence imaging under a fluorescence microscope. Afterwards, the numbers of the adherent *E. coli* on each sample were measured and counted by Image-Pro Plus software and the sterilization rate was calculated from the number of dead bacteria as a percentage of the total.

pFMC micelles & vesicles (for drug delivery): The specific synthetic procedure of pFMC-mPEG (Scheme S6b) is as follows: pFMC (333 mg) was dissolved in 5 mL acetonitrile with thorough stirring to homogenize the solution, and TBDMS-mPEG (670 mg) and TBD (5 mg) were added with continuous stirring. After reacting for 15 min at room temperature, the solution was drip-precipitated into cold ether. The precipitates were then obtained after three redissolution-precipitation cycles. The precipitate, pFMC-mPEG, was finally filtered out and dried under vacuum overnight. The chemical structures, $M_{n, GPC}$, and *PDI* were respectively measured by ¹H NMR and GPC (Figure S16).

Dissolve 50 mg of mPEG-pFMC and pFMC-mPEG in 1 mL DMF with continuous stirring to dissolve fully. The solution was added dropwise to 9 mL deionized water and stirred continuously until the solution was apparently homogeneous. The resulting solutions were dialyzed in deionized water overnight. The mean particle size (*D*) and polydispersity index (*PDI*) of the particles in the aqueous phase were analysed utilizing DLS, and the micromorphology of the particles was observed by TEM.

Crosslinked pFMC hydrogels: The crosslinked pFMC hydrogel was prepared by taking bisTBDMS-PEG as the chemical crosslinking points. The specific synthetic procedure of crosslinked pFMC-PEG (Scheme S6c) is as follows: pFMC (333 mg), bisTBDMS-PEG (2.7 g) and TBD (2 mg) were dissolved in 5 mL acetonitrile with thorough stirring to homogenize the solution. After reacting for 15 min at room temperature, the solution was drip-precipitated into cold ether. The precipitates were then obtained after three redissolution-precipitation cycles. The precipitate, crosslinked pFMC-PEG, was finally filtered out and dried under vacuum overnight.

The dried cross-linked pFMC-PEG was added to the tube and completely immersed in a sufficient amount of 10 mM PBS. The excess PBS was removed from the tube every 6 h by filtering off the solution. And then, fresh PBS was added. The process was repeated until the weight of wet hydrogel no longer increased. After dissolution equilibrium, a sufficient amount of PBS containing 0.1 wt% lipase was added to the pFMC-PEG hydrogels. The equilibrium swelling rate (ESR) of crosslinked pFMC-PEG was calculated from Equation (3).

$$ESR = \frac{wt(w)}{wt(d)} \times 100\% = \frac{wt(wet) - wt(tube)}{wt(dry) - wt(tube)} \times 100\%$$
 Equation (3)

Where *wt(tube)* represents the weight of empty tube; *wt(dry)* represents the total weight of the tube and lyophilized pFMC-PEG; *wt(wet)* represents the total weight of the tube and wet hydrogel after equilibrium swelling.

Electrospun pFMCs (as Tissue Engineering Materials): Drawing on a previous study,¹⁴ the feasibility of blending pFMCs and gelatin for electrospinning was investigated. Dissolve gelatin (6 g) in TFE (34 g) at room temperature and stir until mixture become homogeneous. pFMC (0.6 g) was dissolved in gelatin/TFE solution and stirred intensely. As a verification, the mass fraction of pFMCs was chosen to be 10wt% (relative to the weight of gelatin) in the gelatin-pFMC blend for electrospinning.

After careful wrapping of aluminum foil around the mandrel, the spinning solution was placed in a syringe and placed on a syringe pump. Electrospun membranes of gelatin and gelatin-pFMC blends were fabricated by electrospinning. The electrospun membranes were removed from the aluminum foil and dried overnight in a vacuum oven. The fiber diameter distribution (Figure S17) was obtained by counting *via* Image-Pro Plus software from their SEM images. The element distribution (Figure 3d) and element analysis (Table S4) of the samples were measured by EDS.

The parameters were as follows: distance between needle tip and collector: 26.6 cm, receiving speed: 50 rpm, humidity: 25% RH, temperature: 25°C, and applied voltage: 20 kV. The specific parameters optimized in this study were as follows: 15% gelatin solution: needle size, #22; feed rate, 0.4 mm/min; gelatin-pFMC blend (10 wt% pFMC in 15% gelatin): needle size, #19; feed rate, 0.08 mm/min.

3.7. One-pot strategy combining ROP with SuFEx click chemistry via TBD

To verify the feasibility of one-pot procedure strategies where TBD acted as a coorganocatalyst for the simultaneous ROP and SuFEx click reactions of FMC, a set of validation experiments were designed as follows: FMC was mixed with a silyl ether-protected module in acetonitrile in a glovebox, and then added into initiator/co-organocatalyst, *i.e.*, BnOH/TBD solution. After reacting at room temperature for 1 h, the reaction was terminated by adding an excess of benzoic acid. The polymer was precipitated by dropping the solution into cold methanol, and the precipitate was redissolved-precipitated several times. Then, the precipitate was filtered out and dried under vacuum overnight. In parallel, the SuFEx click reactions of pFMC with the corresponding silyl ether-protected modules catalyzed by TBD were performed.

3.7.1 TBDMS-HDFD as the silyl ether protected module:

Stepwise synthetic strategy of pFMC-HDFD (Scheme S7a): pFMC (333 mg), TBDMS-HDFD (193 mg) and TBD (5 mg) were dissolved in 5 mL acetonitrile with thorough stirring to homogenize the

solution. After reacting for 15 min at room temperature, the solution was drip-precipitated into cold ether. The precipitates were then obtained after three redissolution-precipitation cycles. The precipitate, *pFMC-HDFD, stepwise*, was finally filtered out and dried under vacuum overnight.

One-pot synthetic strategy of pFMC-HDFD (Scheme S8a): FMC (332 mg, 1 mmol), benzyl alcohol (1 mg, 1% mmol), TBDMS-HDFD (193 mg, 0.33 mmol), and TBD (5 mg, 3.5% mmol) was mixed in 5 mL acetonitrile in a glovebox. After reacting at room temperature for 1 h, the reaction was terminated by adding an excess of benzoic acid (8 mg). The polymer was precipitated by dropping the solution into cold methanol, and the precipitate was redissolved-precipitated several times. The precipitate was filtered out and dried under vacuum overnight. Then, *pFMC-HDFD, one-pot* was purified and characterized by demand.

Their chemical structures were confirmed by ¹⁹F NMR (Figure 4a). Moreover, it is possible to evaluate the efficiency of SuFEx PPM (degree of functionality) of these two strategies simply by the quantitative analysis of the ¹⁹F NMR spectrum, illustrated in Equation (4).

The efficiency
$$=\frac{F(c)/17}{F(b)+F(c)}$$
 ÷ feeding ratio × 100% $=\frac{3}{17} \times \frac{F(c)}{F(b)} \times 100\%$ Equation
(4)

Here, F(c) represents the integral area of the fluorine F(c) from HDFD fragments; F(b) represents the integral area of the fluorine F(b) from the residual sulfonyl fluoride in the pFMC; the feeding ratio is the molar ratio of silyl ether protected modules to monomer units of pFMC or FMC at the time of feeding, which are all designed as 1/3 in this experiment.

The efficiencies during the preparation of pFMC-HDFD by stepwise and one-pot procedures were calculated to be ~ 6.0% and 8.7%, respectively

3.7.2 TBDMS-DR1 as the silyl ether protected module:

Stepwise synthetic strategy of pFMC-DR1 (Scheme S7b): pFMC (333 mg), TBDMS-DR1 (143 mg), and TBD (5 mg) reacted according to the above stepwise procedure. Then, *pFMC-DR1*, *stepwise* was purified and characterized by demand.

One-pot synthetic strategy of pFMC-DR1 (Scheme S8b): FMC (332 mg, 1 mmol), benzyl alcohol (1 mg, 1% mmol), TBDMS-DR1 (143 mg, 0.33 mmol), and TBD (5 mg, 3.5% mmol) reacted according to the above one-pot procedure. Then, *pFMC-DR1, one-pot* was purified and characterized by demand.

Their chemical structures were confirmed by ¹H NMR (Figure S18): *e.g.*, δ ppm ~ 8.3 from *aryl-H*(8), ~ 6.8 from *aryl-H*(5), and 3.7 ~ 3.5 from *CH*₂(1,2,4). Moreover, it is possible to evaluate the efficiency of SuFEx PPM (degree of functionality) of these two strategies simply by the quantitative analysis of the ¹H NMR spectrum, illustrated in Equation (5).

The efficiency =
$$\frac{H(5)/2}{H(b)/2}$$
 ÷ feeding ratio × 100% = $\frac{3 \times H(5)}{H(b)} \times 100\%$ Equation (5)

Here, H(5) represents the integral area of the proton H(5) from DR1 fragments; H(b) represents the integral area of the proton H(b) from the pFMCs; the feeding ratio is the molar ratio of silyl ether protected modules to monomer units of pFMC or FMC at the time of feeding, which are all designed as 1/3 in this experiment. The grafting efficiencies during the preparation of pFMC-DR1 by stepwise and one-pot procedures were calculated to be ~ 23.3% and 28.8%, respectively

3.7.3 TBDMS-TPE as the silvl ether protected module:

Stepwise synthetic strategy of pFMC-TPE (Scheme S7c): pFMC (333 mg), TBDMS-TPE (157 mg), and TBD (5 mg) reacted according to the above stepwise procedure. Then, *pFMC-TPE*, *stepwise* was purified and characterized by demand.

One-pot synthetic strategy of pFMC-TPE (Scheme S8c): FMC (332 mg, 1 mmol), benzyl alcohol (1 mg, 1% mmol), TBDMS-TPE (157 mg, 0.33 mmol), and TBD (5 mg, 3.5% mmol) reacted according to the above one-pot procedure. Then, *pFMC-TPE*, *one-pot* was purified and characterized by demand.

Their chemical structures were confirmed by ¹H NMR (Figure S19). The ¹H NMR results showed that the pFMC-TPE synthesized by both strategies showed the characteristic peaks of the tetraphenylene hydrogen (δ 7.1 ~ 6.9 ppm) in the TPE fragment. Moreover, it is possible to evaluate the efficiency of SuFEx PPM (degree of functionality) of these two strategies simply by the quantitative analysis of the ¹H NMR spectrum, illustrated in Equation (6).

The efficiency =
$$\frac{H(2)/19}{H(b)/2}$$
 ÷ feeding ratio × 100% = $\frac{6}{19} \times \frac{H(2)}{H(b)} \times 100\%$ Equation (6)

Here, H(2) represents the integral area of the proton H(2) from TPE fragments; H(b) represents the integral area of the proton H(b) from the pFMCs; the feeding ratio is the molar ratio of silyl

ether protected modules to monomer units of pFMC or FMC at the time of feeding, which are all designed as 1/3 in this experiment.

The grafting efficiencies during the preparation of pFMC-TPE by stepwise and one-pot procedures were calculated to be ~ 8.4% and 13.1%, respectively.

The pFMC, pFMC-TPE stepwise, pFMC-TPE one-pot, and TBDMS-TPE were dissolved in DCM and cast onto clean silicon wafers and observed under natural light (Figure S20a) and black light at 365 nm (Figure S20b), respectively. It can be seen from Figure S20a that there are tape-casting membranes on all silicon wafers except TBDMS-TPE compared to the vacant group. TBDMS-TPE precipitated a white powder on the wafer surface after the solvent evaporated. As shown in Figure S20b, under black light (λ 365 nm), pFMC casting on the wafer shows no fluorescence as well as the blank wafer. The pFMC-TPE from both strategies fluoresce cyan on the wafers, although the fluorescence intensity seems weaker compared to the TBDMS-TPE powder.

In order to verify the AIE of pFMC-TPE, experiments were also designed with different volume ratios of H₂O/THF mixture: 0/1, 1/1, 4/1, 9/1, 19/1. And the mixture components were formulated with water fractions (f_w), *i.e.* 0%, 50%, 80%, 90%, 95%. The photoluminescence (PL) spectra of the two pFMC-TPEs (V = 100 µL, c = 1 mg/L) at an excitation wavelength of 350nm were shown in Figure 4c. The strongest PL intensity of pFMC-TPE synthesized by both strategies could be observed at ~ 475 nm, and the PL intensity was significantly enhanced with the increase of f_w . The AIE phenomenon could be seen more visually in the photographs under UV light at 365 nm (Figure 4, S20c).

4. Computational Methods

Mechanism A:



B3LYP/6-31G(d,p) optimized $\Delta G_{gas}(B3LYP) = -1527.571554 a.u.$ Zero-point energy correction = 0.204203 a.u. SMD(THF)B3LYP-D3/6-311++G(d,p)calculated single-point energies: HF = -1528.2161995 a.u. C 0.11699 1.90555 -0.14371 0 1.15623 0.90675 0.02209 C -1.57516 0.39327 0.95868 C -1.21623 1.20515 -0.12706 C -2.11578 1.37645 -1.1846 C -3.36568 0.75952 -1.1637 C -3.6981 -0.03789 -0.06982 C -2.81427 -0.237 0.99375 H -0.8753 0.247 1.77522 H -1.83871 1.99214 -2.03516 H -4.06395 0.8775 -1.98444 H -3.09595 -0.8776 1.82171 H 0.20388 2.63245 0.67029 H 0.28116 2.44117 -1.08238 S -5.28857 -0.83261 -0.03257 F -6.14535 0.32025 0.7231 0 -5.83403 -0.91585 -1.37404 0 -5.25786 -1.96317 0.87571 C 2.41463 1.38843 0.1386 0 2.6872 2.56813 0.10379 C 3.42461 0.25992 0.32745 C 3.29013 -0.7546 -0.81619 C 4.83342 0.84276 0.19349 H 3.30456 -0.24477 -1.78794 H 2.3675 -1.33191 -0.74259 H 4.92361 1.4276 -0.72768

```
H 5.09007 1.49115 1.03232
C 5.61391 -1.40777 -0.38367
C 3.2074 -0.40583 1.70322
H 3.31334 0.32882 2.50708
H 2.21034 -0.84807 1.7635
H 3.94429 -1.19447 1.86843
O 5.82583 -0.1985 0.18911
O 4.35479 -1.71781 -0.7885
O 6.501 -2.20823 -0.48116
```



B3LYP/6-31G(d,p) optimized $\Delta G_{gas}(B3LYP) = -438.669685 a.u.$ Zero-point energy correction = 0.172080 a.u. SMD(THF)B3LYP-D3/6-311++G(d,p)calculated single-point energies: HF = -439.0046053 a.u. C 0.07128 -0.73684 -0.09018 N 0.01926 0.64967 -0.14517 N-1.15754 -1.39356 -0.07923 N 1.13313 -1.46946 -0.10958 C 1.26407 1.41731 -0.09255 C -1.20596 1.42813 0.01626 C 2.41288 -0.79318 -0.2226 C -2.35728 -0.74159 0.4121 C 2.41222 0.57691 0.46252 C-2.4596 0.61121 -0.28576 H-1.02571 -2.37048 0.14502 H 1.51443 1.79176 -1.09721 H 1.09751 2.29806 0.54159 H -1.15445 2.29791 -0.65231 H-1.2637 1.82681 1.04431 H 2.69174 -0.66963 -1.28303 H 3.18558 -1.43374 0.21953 H-3.2191 -1.371 0.16853

H -2.35607 -0.59781 1.50782 H 3.36092 1.10534 0.31707 H 2.27254 0.43621 1.54104 H -2.55041 0.44514 -1.36424 H -3.34297 1.16322 0.05097



B3LYP/6-31G(d,p) optimized $\Delta G_{gas}(B3LYP) = -346.682698 a.u.$ Zero-point energy correction = 0.101175 a.u. SMD(THF)B3LYP-D3/6-311++G(d,p)calculated single-point energies: HF = -346.9124991 a.u. C-2.30672 -0.31349 -0.04504 C-1.37224 -1.34648 0.03903 C-0.00762 -1.06002 0.09966 C 0.43795 0.26531 0.06994 C-0.50383 1.29666 -0.02351 C-1.86799 1.01155 -0.07552 H-3.36836 -0.53827 -0.09209 H -1.70575 -2.38038 0.05702 H 0.72376 -1.85835 0.15738 H-0.16738 2.33061 -0.05943 H -2.58682 1.82274 -0.1492 C 1.90993 0.5943 0.18127 H 2.14767 0.82931 1.23284 H 2.1242 1.504 -0.4024 0 2.68627 -0.50714 -0.27326 H 3.60567 -0.33956 -0.03309



A-Int1 B3LYP/6-31G(d,p) optimized

 $\Delta G_{gas}(B3LYP) = -1966.239321 a.u.$ Zero-point energy correction = 0.393807 a.u. SMD(THF)B3LYP-D3/6-311++G(d,p) calculated single-point energies: HF = -1967.2309452 a.u. C-4.19028 -1.34007 -0.40742 N -5.27557 -2.13198 -0.0783 N-4.30306 -0.59711 -1.55852 N -3.08537 -1.24705 0.27867 C-5.16329 -3.15371 0.96134 C-6.52675 -2.10642 -0.82859 C-2.98901 -2.06368 1.479 C-5.50603 -0.43116 -2.35578 C-3.70309 -3.40896 1.32233 C-6.73019 -0.755 -1.5057 C-3.36465 2.46209 -0.8657 O -4.27606 2.77455 -1.58721 H -3.52269 0.01654 -1.73664 H -5.72959 -2.84151 1.85273 H-5.6333 -4.07593 0.59301 H-7.34465 -2.3056 -0.12464 H -6.54886 -2.91429 -1.57971 H -3.41017 -1.53727 2.35376 H -1.92835 -2.22545 1.70734 H -5.53966 0.60322 -2.70977 H-5.48878 -1.08779 -3.24068 H -3.64842 -4.00786 2.23789 H-3.21869 -3.97863 0.52059 H -6.86549 0.02163 -0.74498 H-7.63099 -0.78093 -2.12667 O -3.36691 2.77895 0.44356 C -2.43191 2.16326 1.35313 H -2.46562 2.7679 2.25943 H -2.77572 1.14929 1.57533 C -1.03295 2.1283 0.73138 C-1.18258 1.32489 -0.56629 H -0.29981 1.40344 -1.20244 H -1.41051 0.2759 -0.34616

0 -2.27871 1.82724 -1.37521 C-0.48117 3.5488 0.4814 H -0.39717 4.10336 1.42104 H 0.50649 3.50329 0.01557 H -1.14713 4.10683 -0.18037 C-0.10561 1.39066 1.69042 0-0.3427 1.16645 2.85644 0 1.04969 1.02613 1.083 C 1.99414 0.32823 1.91892 H 2.21742 0.9512 2.7931 H 1.53496 -0.59251 2.29102 C 3.24351 0.03631 1.12658 C 4.04051 -1.05466 1.49788 C 3.64523 0.84982 0.05993 C 5.23024 -1.32836 0.82964 H 3.72647 -1.70182 2.31198 C 4.82792 0.58525 -0.62572 H 3.02224 1.68328 -0.24254 C 5.61062 -0.49856 -0.22596 H 5.84527 -2.17807 1.10307 H 5.13783 1.19957 -1.46355 S 7.12427 -0.83915 -1.09075 07.53282 -2.21228 -0.86066 07.08977 -0.24199 -2.41255 F 8.14481 0.07634 -0.22028



A-TS1 B3LYP/6-31G(d,p) optimized $\Delta G_{gas}(B3LYP) = -1966.199408 a.u.$ Zero-point energy correction = 0.398933 a.u. SMD(THF)B3LYP-D3/6-311++G(d,p) calculated single-point energies: HF = -1967.2072892 a.u. C -4.50441 1.05314 -0.0895 N -5.52113 1.59531 -0.81713

N -3.65558 1.81654 0.58208 N-4.30404 -0.29819 -0.08147 C-6.67461 0.82079 -1.29024 C-5.6389 3.04637 -1.00927 C-5.22623 -1.13028 -0.8719 C-3.83336 3.2523 0.68468 C-6.64971 -0.59951 -0.74447 C-4.35215 3.78408 -0.64994 C-3.8592 -0.93833 1.24316 0-4.52038-0.717512.23133 H -2.88581 1.20479 1.10576 H -6.66713 0.81127 -2.38957 H -7.58615 1.34628 -0.97775 H-5.9099 3.22698 -2.05714 H -6.47166 3.41599 -0.39348 H-4.90881 -1.13353 -1.92346 H-5.14277 -2.14901 -0.49631 H -2.86713 3.69548 0.93959 H-4.5315 3.50568 1.49603 H-7.35835 -1.22006 -1.30138 H -6.93578 -0.61467 0.31212 H -3.59356 3.61954 -1.42268 H -4.55313 4.85845 -0.60167 0 -2.21368 0.03378 1.49665 C-1.16215 -0.25548 0.63127 H -0.22499 0.19153 1.00198 H -1.32853 0.1498 -0.38859 C-0.97968 -1.79683 0.5149 C-2.31934 -2.38642 0.03971 H-2.24439 -3.46813 -0.09168 H-2.59401 -1.94725 -0.92518 O -3.36073 -2.19977 1.00401 C-0.56101 -2.38888 1.87486 H-0.49311 -3.48119 1.82889 H 0.41008 -1.99532 2.18456 H -1.30691 -2.11513 2.6216 C 0.05522 -2.10332 -0.55337 0-0.14609 -2.69608 -1.59373 O 1.28186 -1.61016 -0.22731 C 2.3169 -1.83815 -1.19184 H 2.53689 -2.91068 -1.24449 H 1.95795 -1.54243 -2.1845 C 3.55018 -1.05593 -0.81089 C 3.52662 -0.06177 0.1734 C 4.74555 -1.31816 -1.49632 C 4.6782 0.66335 0.47391 H 2.60431 0.14121 0.70359 C 5.90246 -0.60175 -1.212 H 4.77091 -2.08799 -2.26296 C 5.85368 0.38338 -0.22249 H 4.66557 1.44236 1.22783 H 6.82589 -0.79101 -1.74729 S 7.3233 1.30403 0.15081 0 8.25207 1.23593 -0.96265 0 6.98074 2.55233 0.80715 F 7.95841 0.35858 1.30924



A-Int2

B3LYP/6-31G(d,p) optimized $\Delta G_{gas}(B3LYP) = -1966.239921 a.u.$ Zero-point energy correction = 0.397609 a.u. SMD(THF)B3LYP-D3/6-311++G(d,p) calculated single-point energies: HF = -1967.2377816 a.u. C 5.2944 0.74771 0.15914 N 6.30359 1.38 -0.54065 N 4.32066 1.31742 0.77559 N 5.40554 -0.67163 0.15115 C 7.49711 0.6381 -0.93979 H 7.33251 0.10441 -1.88752 H 8.30155 1.35969 -1.10682 C 6.33758 2.84177 -0.5847 H 6.8061 3.13937 -1.52926

H 6.96189 3.24232 0.23001 C 6.71471 -1.33517 0.35083 H 6.7859 -2.14061 -0.38475 H 6.73949 -1.80544 1.33915 C 4.21911 2.77523 0.72485 H 3.15613 3.03609 0.73188 H 4.64544 3.18816 1.65123 C 7.86154 -0.34477 0.16995 H 8.77829 -0.89349 -0.06773 H 8.04434 0.21933 1.09159 C 4.91837 3.39165 -0.48843 H 4.3687 3.13401 -1.40094 H 4.94369 4.48362 -0.41413 H 2.52975 0.82022 1.08161 0 1.57146 1.03312 1.15738 C 4.33277 -1.55189 0.11603 0 4.47106 -2.74418 0.32143 C 0.79875 -0.13218 1.21354 H 1.11814 -0.8091 2.02378 H-0.2245 0.18458 1.439 C 2.01871 -1.83931 -0.25167 H 2.01979 -2.40136 -1.19074 H 2.08495 -2.55846 0.56514 C 0.76672 -0.95715 -0.12494 C 0.62653 -0.00265 -1.32694 H 0.58891 -0.56026 -2.26875 H -0.28097 0.59847 -1.24403 H 1.48237 0.67201 -1.34644 C-0.41895 -1.91656 -0.06783 0-0.34837 -3.12609 -0.00657 O -1.60925 -1.26012 -0.08165 C-2.77312 -2.09715 -0.01777 H -2.73981 -2.68892 0.90511 H-2.75594 -2.81016 -0.84865 C-4.01612 -1.24265 -0.06302 C-3.97949 0.13849 0.15859 C-5.24642 -1.86756 -0.31408 C -5.15314 0.88969 0.1358

```
H -3.02922 0.62615 0.33823
C -6.42718 -1.13398 -0.33674
H -5.28075 -2.93739 -0.50141
C -6.36436 0.24255 -0.10717
H -5.13214 1.96226 0.29224
H -7.37903 -1.60901 -0.54517
S -7.86299 1.19217 -0.13976
O -7.56279 2.59737 -0.34282
O -8.88188 0.49217 -0.90034
F -8.30885 1.05831 1.41686
O 3.1683 -0.96746 -0.22303
```



A-Int3

B3LYP/6-31G(d,p) optimized $\Delta G_{gas}(B3LYP) = -2312.919460 a.u.$ Zero-point energy correction = 0.518775 a.u. SMD(THF)B3LYP-D3/6-311++G(d,p) calculated single-point energies: HF = -2314.1675813 a.u. C-4.46773 -1.8885 0.45015 N -5.15327 -3.04365 0.72383 N -3.74598 -1.21169 1.28552 N-4.61684 -1.44127 -0.88638 C-6.10921 -3.56565 -0.25081 H-5.59346 -4.11552 -1.05088 H -6.76351 -4.27186 0.26664 C-5.09859 -3.62987 2.06517 H-5.16459 -4.71794 1.95804 H -5.96504 -3.30577 2.66168 C-5.94953 -1.43391 -1.53439 H-5.7988 -1.73597 -2.5735 H-6.34556 -0.41352 -1.55456 C-3.61285 -1.71612 2.65531

H -2.62299 -1.42806 3.02051 H-4.35092 -1.20745 3.29269 C-6.90539 -2.39541 -0.82586 H-7.66455 -2.74182 -1.5339 H-7.42815 -1.89455 -0.0035 C -3.79461 -3.23149 2.7496 H -2.95326 -3.72859 2.2543 H -3.80628 -3.55956 3.79362 H -1.73547 -1.29178 0.87996 0-0.80151 -1.4157 1.12829 C-3.62662 -0.77163 -1.60728 0-3.89033 -0.07877 -2.57052 C-0.04059 -0.44737 0.43769 H -0.40918 0.56907 0.63431 H 0.97961 -0.52516 0.82206 C-1.33318 -0.24855 -1.76335 H-1.31805 -0.40029 -2.84438 H -1.55574 0.79871 -1.55571 C-0.00752 -0.67577 -1.11103 C 0.32429 -2.15024 -1.42338 H 0.34288 -2.32887 -2.50355 H 1.29735 -2.42448 -1.00982 H-0.43208 -2.79157 -0.9703 C 1.06393 0.22664 -1.71931 0 0.87922 1.07334 -2.56667 0 2.29657 -0.02677 -1.20303 C 3.35858 0.78061 -1.72896 H 3.13147 1.83793 -1.55009 H 3.40909 0.65031 -2.81595 C 4.66532 0.39438 -1.0799 C 4.74975 -0.59221 -0.09197 C 5.83148 1.05543 -1.49432 C 5.97843 -0.91527 0.48191 H 3.85299 -1.11023 0.2241 C 7.06448 0.74564 -0.93287 H 5.7753 1.81718 -2.26739 C 7.12124 -0.23932 0.0567 H 6.05393 -1.68697 1.23967

H 7.97052 1.24368 -1.25864 S 8.6884 -0.64413 0.78294 0 8.63192 -1.95652 1.39993 0 9.76778 -0.24084 -0.09966 F 8.70729 0.41832 2.0119 0-2.38642 -1.05802 -1.18171 C-3.64902 3.7035 0.60764 C-2.66989 4.04328 1.54695 C-2.38654 5.3817 1.82184 C -3.08099 6.39842 1.16394 C -4.05719 6.06711 0.22251 C-4.33382 4.72843 -0.05564 H -2.12855 3.24569 2.04412 H -1.62012 5.63164 2.55068 H -2.85895 7.44018 1.37744 H -4.59595 6.85082 -0.30298 H -5.08541 4.47626 -0.8007 C-3.99851 2.25437 0.33907 H-4.8541 1.9738 0.97675 H -4.33849 2.15172 -0.70378 0 -2.89433 1.40523 0.59882 H -3.22887 0.52577 0.88804



A-Int4

B3LYP/6-31G(d,p) optimized $\Delta G_{gas}(B3LYP) = -2312.913583 a.u.$ Zero-point energy correction = 0.517440 a.u. SMD(THF)B3LYP-D3/6-311++G(d,p) calculated single-point energies: HF = -2314.160201 a.u. C 4.44448 1.7263 0.1825 N 4.91893 3.01746 0.08331 N 4.94952 0.77898 0.8881 N 3.31697 1.43269 -0.632 C 4.34858 4.08852 -0.73814 C 6.15147 3.38393 0.78911 C 3.17954 2.20733 -1.8725 C 6.07999 1.08624 1.75349 C 3.07513 3.67793 -1.4776 C 6.98546 2.15361 1.13826 C 2.29037 0.64233 -0.13739 0 2.1598 0.30402 1.02712 H 4.39118 -0.95142 0.48276 H 5.11395 4.38964 -1.46979 H 4.16048 4.96534 -0.10353 H 6.72158 4.06397 0.14357 H 5.89531 3.94647 1.69886 H 4.05402 2.02748 -2.50943 H 2.29812 1.85934 -2.40331 H 6.63501 0.15897 1.92308 H 5.71215 1.42006 2.73541 H 2.94429 4.31926 -2.35516 H 2.19389 3.80479 -0.84014 H 7.44846 1.74995 0.23077 H 7.79199 2.43915 1.82105 0 4.14976 -1.7993 0.03847 C 5.16544 -2.0843 -0.8934 H 4.81458 -2.94142 -1.48486 H 5.31366 -1.2561 -1.60774 C 0.41289 -0.67133 -0.81882 H 0.76505 -1.29691 0.0021 H 0.3571 -1.2784 -1.72208 C-0.98044 -0.06191 -0.52097 C -1.13134 0.40912 0.96328 H-0.94528 -0.44932 1.62646 H-2.1676 0.72502 1.11422 0-0.31378 1.50578 1.29521 H 0.57792 1.1526 1.46772 C 6.50932 -2.43333 -0.26924 C 6.58257 -2.89804 1.0486 C 7.69174 -2.32497 -1.01178 C 7.81167 -3.24881 1.61081

H 5.6636 -2.97434 1.62073 C 8.92054 -2.68045 -0.45483 H 7.65002 -1.95765 -2.03551 C 8.98464 -3.14356 0.86114 H 7.85278 -3.60784 2.6358 H 9.82865 -2.59022 -1.04499 H 9.94076 -3.41715 1.29834 C-1.98355 -1.19722 -0.73666 O -1.70849 -2.34167 -1.02812 O -3.26425 -0.7872 -0.54071 C-1.29069 1.11058 -1.47298 H -1.13102 0.83055 -2.51915 H-2.32632 1.43698 -1.35617 H-0.63605 1.94814 -1.22888 C-4.26575 -1.805 -0.69737 H-4.04231 -2.63446 -0.01596 H-4.21637 -2.21046 -1.71346 C-5.62974 -1.22659 -0.41079 C-5.7984 0.00464 0.23214 C-6.75955 -1.96959 -0.78307 C-7.07548 0.48962 0.50767 H -4.92855 0.58786 0.50792 C-8.04083 -1.50316 -0.51105 H-6.63672 -2.91986 -1.29561 C-8.182 -0.27404 0.13723 H -7.21519 1.44926 0.99241 H-8.9182 -2.06663 -0.80733 S-9.81163 0.33576 0.48703 0-9.777 1.77287 0.68527 0-10.7834 -0.31248 -0.37425 F-10.03455 -0.30633 1.96233 0 1.4201 0.32185 -1.1184



A-TS2

B3LYP/6-31G(d,p) optimized $\Delta G_{gas}(B3LYP) = -2312.881961 a.u.$ Zero-point energy correction = 0.519888 a.u. SMD(THF)B3LYP-D3/6-311++G(d,p) calculated single-point energies: HF = -2314.131307 a.u. C 4.78603 -1.99223 -0.05238 N 5.2122 -3.25881 0.20847 N 5.47089 -1.14644 -0.79527 N 3.62369 -1.54466 0.52454 C 4.36811 -4.30368 0.80327 C 6.53076 -3.71681 -0.24504 C 2.99042 -2.38563 1.54812 C 6.68121 -1.5599 -1.48164 C 2.94016 -3.82605 1.04795 C 7.44891 -2.55205 -0.60773 C 2.79684 -0.60237 -0.26179 0 2.53822 -0.84802 -1.44303 H 4.95487 -0.08324 -0.77402 H 4.83192 -4.61614 1.74975 H 4.38041 -5.17605 0.13682 H 6.97163 -4.32109 0.55758 H 6.39662 -4.38092 -1.11111 H 3.56386 -2.31766 2.48205 H 1.99932 -1.98402 1.73713 H 7.27846 -0.66636 -1.68177 H 6.44072 -2.0126 -2.45474 H 2.45902 -4.48393 1.77838 H 2.34628 -3.85716 0.12932 H 7.78698 -2.04379 0.3018
H 8.33403 -2.93647 -1.12345 0 4.073 0.81499 -0.43302 C 4.46762 1.45358 0.75447 H 3.59659 1.54669 1.42224 H 5.21175 0.85137 1.30941 C 0.88348 0.78487 0.01382 H 1.18014 1.0561 -0.99955 H 0.85135 1.69154 0.62031 C -0.51161 0.10849 0.03084 C -0.6814 -0.95754 -1.1046 H -0.54456 -0.45789 -2.07584 H -1.7096 -1.3314 -1.06579 0 0.17308 -2.06852 -0.97691 H 1.05108 -1.77756 -1.30454 C 5.05113 2.83545 0.503 C 4.88875 3.4725 -0.73071 C 5.74383 3.50253 1.52178 C 5.4073 4.75213 -0.94082 H 4.35763 2.94599 -1.51613 C 6.25909 4.78161 1.31538 H 5.88231 3.01496 2.48508 C 6.09233 5.41206 0.07986 H 5.27463 5.23471 -1.90559 H 6.79459 5.28499 2.11597 H 6.49549 6.4074 -0.08461 C -1.51913 1.22071 -0.25804 O -1.2492 2.36142 -0.56806 0 -2.80429 0.78315 -0.15945 C -0.80148 -0.54233 1.39755 H -0.57806 0.13974 2.22396 H -1.8492 -0.84167 1.4688 H -0.18328 -1.43467 1.50134 C -3.81206 1.76583 -0.4441 H -3.68912 2.11548 -1.47662 H -3.6674 2.63689 0.20263 C -5.17831 1.15843 -0.24107 C -5.38646 -0.22537 -0.27997 C -6.27146 2.01257 -0.03827

C -6.66596 -0.75358 -0.12393
H -4.54197 -0.88931 -0.41971
C -7.55667 1.50286 0.11399
H -6.11567 3.08677 0.0098
C -7.73777 0.11907 0.06595
H -6.83313 -1.82466 -0.13727
H -8.40307 2.1577 0.28688
S -9.3708 -0.54597 0.26614
O -9.29959 -1.94074 0.66062
O -10.22363 0.41507 0.94109
F -9.85788 -0.55162 -1.28389
O 1.90487 -0.03925 0.60738



B-Int1

B3LYP/6-31G(d,p) optimized $\Delta G_{gas}(B3LYP) = -2312.925615 a.u.$ Zero-point energy correction = 0.516102 a.u. SMD(THF)B3LYP-D3/6-311++G(d,p) calculated single-point energies: HF = -2314.14.1637973 a.u. C 4.96433 -2.31016 0.23715 N 5.75349 -3.44405 0.22457 N 4.47257 -1.88419 -0.9649 N 4.63734 -1.64402 1.31457 C 6.45019 -3.88398 1.43312 H 5.96615 -4.79077 1.82808 H 7.47445 -4.16761 1.15491 C 6.06877 -4.20087 -0.98614 H 6.03904 -5.27034 -0.73746 H 7.10186 -3.97926 -1.3013 C 5.07856 -2.16629 2.59606 H 4.37061 -2.92059 2.981

H 5.0788 -1.34694 3.32334 C 4.93169 -2.38515 -2.2438 H 4.18546 -2.11226 -2.99209 H 5.885 -1.92337 -2.55163 C 6.47229 -2.78929 2.49622 H 6.79846 -3.21258 3.45228 H 7.19056 -2.01147 2.21247 C 5.10262 -3.89645 -2.12786 H 4.1277 -4.3537 -1.92718 H 5.49298 -4.32343 -3.05714 H 3.93076 -1.02828 -0.94759 H 3.65718 -0.31379 1.02639 0 3.13745 0.47081 0.66401 C 4.01073 1.58168 0.56226 H 4.22132 1.80486 -0.49256 H 4.97614 1.33946 1.03444 0 0.96117 -0.0352 -2.34523 C 2.05671 0.75505 -2.34401 0 3.14017 0.29676 -2.61493 C -0.35544 0.52569 -2.22102 H -0.67962 0.88547 -3.20633 C-0.37241 1.66146 -1.1895 C 0.66891 2.67882 -1.66652 H 0.30571 3.2229 -2.54277 H 0.9214 3.40027 -0.88841 H-0.99866 -0.30281 -1.92365 C 3.43044 2.81797 1.22314 C 2.69248 2.71279 2.40906 C 3.63735 4.08868 0.67328 C 2.18293 3.85035 3.03506 H 2.51258 1.72503 2.82171 C 3.13076 5.23077 1.29841 H 4.19546 4.18278 -0.2554 C 2.40171 5.11515 2.48269 H 1.61391 3.75162 3.95591 H 3.29975 6.20892 0.85619 H 2.00338 6.00132 2.96868 0 1.92136 2.05205 -2.0268

C -1.73874 2.34071 -1.20115 0-1.93453 3.52359 -1.37324 O -2.73394 1.44837 -0.97695 C-4.06696 2.00221 -0.92891 H-4.0655 2.85617 -0.24246 H-4.33667 2.38378 -1.91817 C-5.02451 0.93128 -0.47257 C -6.30967 0.87437 -1.02499 C-4.66772 0.02677 0.53674 C-7.23552 -0.06631 -0.58016 H -6.59249 1.57163 -1.80837 C-5.57666 -0.92573 0.98716 H -3.67286 0.06739 0.9661 C -6.85219 -0.96 0.4198 H-8.23625 -0.10842 -0.99469 H-5.31276 -1.62364 1.77366 S-8.02041 -2.17171 0.98826 0-7.64161 -2.65155 2.30399 0 -9.37092 -1.75077 0.6656 F-7.67843 -3.38205 -0.03878 C -0.06796 1.13946 0.2321 H-0.14161 1.9556 0.95704 H -0.78047 0.35832 0.51043 H 0.9475 0.73905 0.29652



B-TS1

B3LYP/6-31G(d,p) optimized $\Delta G_{gas}(B3LYP) = -2312.893159 a.u.$ Zero-point energy correction = 0.517389 a.u. SMD(THF)B3LYP-D3/6-311++G(d,p) calculated single-point energies: HF = -2314.1326602 a.u. C 5.78775 -1.08607 -0.12641 N 7.0382 -1.60942 0.11891 N 5.0825 -1.59589 -1.17045 N 5.25039 -0.12967 0.5978 C 7.95098 -0.98917 1.0815 H 8.04638 -1.64234 1.96226 H 8.94654 -0.92968 0.62093 C 7.59221 -2.7478 -0.61302 H 8.12526 -3.38558 0.10435 H 8.34159 -2.39196 -1.33845 C 5.96977 0.33697 1.77248 H 5.77856 -0.31784 2.63862 H 5.58089 1.32549 2.03685 C 5.60994 -2.58059 -2.09354 H 4.76338 -3.10085 -2.54948 H 6.17812 -2.10821 -2.91135 C 7.47247 0.39771 1.50044 H 8.03221 0.72653 2.38207 H 7.66135 1.11807 0.69654 C 6.51105 -3.54825 -1.33181 H 5.91079 -4.10666 -0.60537 H 6.98013 -4.26862 -2.0092 H 4.11194 -1.28923 -1.28587 H 3.97963 0.49469 0.32264 O 3.06934 1.0456 0.07734 C 3.39901 1.9914 -0.94097 H 2.85963 1.71134 -1.85559 H 4.47074 1.91616 -1.16803 0 2.01572 -1.0472 0.61966 C 1.91347 -0.30057 -0.55794 O 2.37584 -0.71659 -1.61693 C 0.91785 -1.95638 0.75208 H 0.92656 -2.6841 -0.06927 C-0.41376 -1.17527 0.7652 C-0.42326 -0.29345 -0.50852 H-0.49178 -0.91918 -1.40998 H-1.2614 0.40519 -0.50552 H 1.07313 -2.49471 1.68852

C 3.05788 3.40751 -0.52819 C 3.87553 4.47281 -0.9206 C 1.90566 3.67996 0.21952 C 3.54836 5.78748 -0.58291 H 4.77818 4.27305 -1.49409 C 1.58099 4.99171 0.5636 H 1.27431 2.85255 0.5249 C 2.39925 6.05067 0.16278 H 4.19534 6.60282 -0.89488 H 0.68521 5.18997 1.14618 H 2.1444 7.07168 0.4325 0 0.76385 0.49922 -0.55788 C-0.51259 -0.29691 2.03058 H-1.4287 0.29983 2.02497 H-0.50687-0.9144 2.93448 H 0.34752 0.37399 2.06362 C-1.56424 -2.16784 0.73787 0-1.47222 -3.36074 0.93108 O -2.75048 -1.5551 0.48139 C-3.89896 -2.41998 0.4638 H-3.76728 -3.18501 -0.30817 H-3.9611 -2.94648 1.42376 C-5.14374 -1.60481 0.21557 C-5.19212 -0.22934 0.47056 C-6.29275 -2.25929 -0.25004 C -6.37094 0.48604 0.27221 H-4.30121 0.28248 0.81387 C-7.48009 -1.56201 -0.44671 H -6.25817 -3.3234 -0.4668 C-7.50397 -0.19204 -0.17784 H -6.41263 1.55429 0.45261 H-8.36851 -2.05978 -0.8182 S -9.01356 0.70924 -0.42283 0-8.73351 2.12449 -0.57739 0 -9.89029 -0.01872 -1.32141 F-9.66837 0.54936 1.05521



B-Int2

B3LYP/6-31G(d,p) optimized $\Delta G_{gas}(B3LYP) = -2312.917762 a.u.$ Zero-point energy correction = 0.524196 a.u. SMD(THF)B3LYP-D3/6-311++G(d,p)calculated single-point energies: HF = -2314.1614565 a.u. C-5.18616 -0.84518 0.15449 N -6.47971 -1.11835 0.54986 N-4.8645 -0.25455 -0.96639 N-4.17911 -1.26531 0.98443 C -6.82613 -1.80258 1.7957 H -7.20934 -1.06706 2.52169 H-7.65052 -2.49712 1.58661 C-7.62064 -0.60275 -0.20863 H-8.36844 -0.23682 0.50746 H-8.09176 -1.42477 -0.769 C-4.41319 -1.65331 2.36205 H -4.56397 -0.78326 3.02273 H-3.52654 -2.18285 2.72159 C-5.9319 0.0853 -1.89443 H-5.57469 0.8907 -2.54558 H -6.16317 -0.76705 -2.55496 C-5.64275 -2.55507 2.39656 H-5.88522 -2.85525 3.42065 H -5.43664 -3.46087 1.81669 C-7.20087 0.51489 -1.15826 H -6.99377 1.42777 -0.58811 H-8.01826 0.7332 -1.85349 H -3.39338 0.25705 -1.39673 H-3.24881 -0.94961 0.72442

0-1.4318 -0.70748 -0.1434 C-1.09814 -1.7533 -1.07154 H-1.09888 -1.35997 -2.09027 H-1.90362 -2.49666 -1.00742 0-1.98461 1.33901 0.40306 C -1.58721 0.56577 -0.70922 0 -2.48269 0.60213 -1.73436 C-2.11524 2.72251 0.07721 H -2.91555 2.86356 -0.65958 H-2.3759 3.22803 1.00771 C -0.79554 3.28109 -0.49172 C-0.35287 2.34653 -1.6328 H -1.04737 2.44797 -2.47471 H 0.65847 2.57352 -1.96949 O -0.32911 0.9889 -1.18353 C-0.99942 4.71712 -1.01441 H -1.32885 5.37988 -0.20888 H-0.06972 5.11952 -1.42873 H -1.75725 4.72985 -1.80387 C 0.23093 3.34346 0.64706 0-0.03758 3.61443 1.79635 0 1.49462 3.12972 0.20476 C 2.5462 3.13264 1.1859 H 3.0163 4.12192 1.19056 H 2.10211 2.96948 2.17321 C 3.55098 2.05922 0.8468 C 4.90028 2.2557 1.16787 C 3.14524 0.85026 0.26504 C 5.84273 1.26137 0.92283 H 5.21913 3.19328 1.615 C 4.07604 -0.1537 0.00924 H 2.10296 0.69458 0.00579 C 5.41449 0.0662 0.34246 H 6.88731 1.40045 1.17647 H 3.76288 -1.09707 -0.42307 S 6.61014 -1.2062 0.0299 O 7.82961 -0.9429 0.77305 0 5.97527 -2.51198 0.02086

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F 6.96504-0.88505-1.5236C 0.22946-2.39702-0.73748C 0.94826-3.05855-1.74025C 0.73381-2.396250.56794C 2.14719-3.70948-1.44643H 0.57137-3.05758-2.76053C 1.93393-3.045420.86247H 0.18832-1.868551.34308C 2.64585-3.70555-0.14189H 2.69828-4.20993-2.23748H 2.31897-3.030941.87827H 3.5893-4.191350.08498
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B-Int3

B3LYP/6-31G(d,p) optimized $\Delta G_{gas}(B3LYP) = -2312.918794 a.u.$ Zero-point energy correction = 0.524348 a.u. SMD(THF)B3LYP-D3/6-311++G(d,p)calculated single-point energies: HF = -2314.1632878 a.u. C-4.53688 -0.69578 0.35471 N-5.67678 -1.3457 0.77979 N-4.36859 -0.20112 -0.84357 N -3.50108 -0.59952 1.25001 C-5.83914 -1.91907 2.11586 H -6.48774 -1.26481 2.72096 H -6.36548 -2.87715 2.01397 C-6.8672 -1.40229 -0.06947 H-7.74673 -1.2407 0.56739 H-6.96647 -2.40999 -0.50117 C-3.65932 -0.86579 2.6671

H-4.13704 -0.02667 3.20103 H-2.66446 -1.00189 3.09982 C-5.42755 -0.39152 -1.82373 H -5.33724 0.39431 -2.58173 H-5.3001 -1.34937 -2.35515 C -4.50387 -2.12547 2.82353 H-4.6821 -2.35212 3.87914 H-3.96891 -2.97189 2.38011 C-6.81121 -0.35283 -1.17496 H -6.98173 0.64268 -0.74907 H-7.60448 -0.54386 -1.90517 H-3.02454 0.49583 -1.42886 H -2.74538 0.01498 0.95966 0-0.67427 -0.28202 -0.65241 C-0.39899 -1.16597 -1.75395 H-1.3247 -1.33391 -2.31609 H 0.32778 -0.70283 -2.4302 0 -1.53388 1.50974 0.2651 C-1.17113 0.96557 -1.00777 0-2.2179 0.95432 -1.87468 C -1.94611 2.87628 0.17597 H -2.84225 2.96149 -0.45 H -2.17332 3.19327 1.19471 C-0.81409 3.73664 -0.42126 C-0.4046 3.08212 -1.75169 H -1.22296 3.19317 -2.47342 H 0.49972 3.53297 -2.16207 O -0.10628 1.69932 -1.56241 C 0.14018 -2.45382 -1.1848 C-0.60803 -3.17835 -0.24663 C 1.38917 -2.94403 -1.57878 C-0.11334 -4.36905 0.28142 H-1.56954 -2.78972 0.07719 C 1.88918 -4.13628 -1.04806 H 1.97822 -2.38786 -2.30414 C 1.13661 -4.85119 -0.11759 H-0.70008 -4.92236 1.00974 H 2.8701 -4.49114 -1.34766

H 1.52422 -5.7752 0.30138 C-1.30156 5.18043 -0.6466 H -1.59397 5.63991 0.30137 H -0.51461 5.79569 -1.09472 H -2.16381 5.19102 -1.32044 C 0.32128 3.77591 0.61197 0 0.1413 4.00308 1.78875 0 1.54133 3.57236 0.06116 C 2.67101 3.50786 0.9495 H 3.30221 4.37847 0.74454 H 2.30769 3.58171 1.97932 C 3.44308 2.22705 0.73189 C 4.81172 2.20384 1.03419 C 2.81204 1.05855 0.28576 C 5.55235 1.03465 0.89671 H 5.30506 3.10836 1.37997 C 3.54079 -0.12066 0.14089 H 1.75777 1.06698 0.03195 C 4.90329 -0.11632 0.44426 H 6.60947 1.00775 1.13511 H 3.05419 -1.03162 -0.19056 S 5.84832 -1.60183 0.23297 07.05236 -1.55147 1.04344 0 4.97838 -2.76358 0.20445 F 6.34875 -1.39655 -1.30175



B-TS2

B3LYP/6-31G(d,p) optimized $\Delta G_{gas}(B3LYP) = -2312.906126 a.u.$ Zero-point energy correction = 0.519600 a.u. SMD(THF)B3LYP-D3/6-311++G(d,p) calculated single-point energies: HF = -2314.1520917 a.u. C-4.37399 -2.03674 0.55301 N -5.37247 -2.9183 0.85271 N -3.56692 -1.58292 1.52729 N-4.17495 -1.60697 -0.69154 C-6.33741 -3.36312 -0.15865 H-6.07772 -4.37878 -0.49161 H -7.32063 -3.42309 0.32289 C-5.56009 -3.4615 2.20161 H -5.85214 -4.51321 2.09911 H -6.39442 -2.94116 2.69545 C-4.96004 -2.11316 -1.80645 H-4.50579 -3.02411 -2.2258 H-4.94468 -1.35508 -2.59411 C-3.75116 -1.92019 2.92884 H-2.78233 -1.82202 3.42515 H-4.44095 -1.21651 3.41954 C-6.38429 -2.40699 -1.34667 H -6.97383 -2.85389 -2.15262 H-6.8725 -1.47121 -1.05315 C-4.28922 -3.34266 3.03764 H -3.53464 -4.04685 2.67112 H-4.51099 -3.59738 4.07803 H-2.8751 -0.83319 1.29613 H-3.24946 -1.00878 -0.93055 0 -2.69258 1.88795 -0.39003 C-3.88228 1.92383 0.38954 H-4.55324 1.10684 0.08986 H -3.62427 1.76725 1.44411 0-2.05053 -0.33368 -1.27276 C -1.73345 0.99053 -0.00025 0 -1.76637 0.40219 1.10427 C 0.53691 0.57314 -0.452 H 0.61324 0.15432 0.55844 H 1.43026 1.16272 -0.66653 C-0.99705 -1.26051 -1.21619 H-0.93101 -1.75153 -0.22933

H-1.14638 -2.05841 -1.9584 C 0.35262 -0.5533 -1.49638 C 0.3626 0.03506 -2.92482 H 1.29248 0.57583 -3.12508 H 0.25366 -0.75927 -3.67057 H-0.47997 0.72101 -3.02086 C 1.47379 -1.57365 -1.38374 0 1.34904 -2.77775 -1.4504 0 2.69315 -0.97862 -1.23112 C 3.81464 -1.87262 -1.16685 H 3.98785 -2.3131 -2.15477 H 3.57365 -2.69972 -0.48897 C 5.03189 -1.12062 -0.68979 C 6.30381 -1.57673 -1.06141 C 4.92105 -0.00597 0.15113 C 7.45308 -0.94705 -0.59349 H 6.39782 -2.42919 -1.72834 C 6.05988 0.64159 0.62267 H 3.93866 0.36071 0.42438 C 7.31461 0.15715 0.24925 H 8.43933 -1.28783 -0.88718 H 5.98186 1.51446 1.26098 S 8.77229 0.969 0.85255 0 9.91019 0.64751 0.01072 0 8.46038 2.32627 1.26036 F 8.99872 0.13817 2.23094 O -0.55183 1.48866 -0.51075 C-4.57013 3.25618 0.19744 C-3.85158 4.404 -0.15432 C-5.948 3.36174 0.42095 C-4.50116 5.6331 -0.27488 H-2.78753 4.31829 -0.34479 C-6.59677 4.59139 0.30819 H -6.51921 2.47363 0.6837 C-5.87364 5.73304 -0.04126 H -3.93217 6.51566 -0.55382 H-7.66698 4.6562 0.4844 H -6.37699 6.69093 -0.1362



B3LYP/6-31G(d,p) optimized $\Delta G_{gas}(B3LYP) = -2312.908266 a.u.$ Zero-point energy correction = 0.520424 a.u. SMD(THF)B3LYP-D3/6-311++G(d,p) calculated single-point energies: HF = -2314.1583859 a.u. C-4.97857 -1.50535 -0.54703 N -6.22334 -2.06834 -0.50092 N-4.03255 -2.04386 -1.32743 N-4.68963 -0.4237 0.17499 C-7.34297 -1.42768 0.19594 H-7.54399 -1.96727 1.13335 H-8.23481 -1.53462 -0.43395 C-6.53777 -3.32982 -1.17723 H-7.19188 -3.91014 -0.51499 H-7.11067 -3.12112 -2.09331 C -5.66345 0.17909 1.07093 H-5.62964 -0.29438 2.06436 H-5.38537 1.2284 1.19699 C-4.27108 -3.19466 -2.18099 H-3.3107 -3.69196 -2.33758 H-4.64333 -2.88408 -3.16905 C-7.06275 0.04483 0.47821 H -7.82095 0.43607 1.16312 H-7.11829 0.62309 -0.4502 C-5.27794 -4.12305 -1.50949 H-4.84 -4.53199 -0.59263 H-5.53648 -4.96158 -2.1629 H-3.06583 -1.63785 -1.31473 H -3.70963 0.06701 0.10007 0 -2.43898 0.85607 0.0542

C-2.50993 1.75234 -1.0187 H -1.49434 2.07413 -1.30957 H -2.92948 1.27744 -1.92401 0 -1.39045 -1.28426 0.77614 C-1.17205 -0.54386 -0.37076 O -1.53875 -1.03826 -1.44045 C-1.07061 -0.69364 2.0372 H-1.12467 -1.5049 2.76524 C 0.32955 -0.06828 2.02016 C 0.36613 0.87114 0.80901 H 1.36801 1.26228 0.62736 H-0.32902 1.69879 0.98303 H -1.80811 0.07929 2.27428 C-3.32999 2.99423 -0.7002 C-3.56513 3.38658 0.6229 C-3.84289 3.79171 -1.73241 C-4.29233 4.545 0.90848 H -3.16829 2.76524 1.41914 C-4.56468 4.95162 -1.45206 H -3.67478 3.49765 -2.76647 C-4.79427 5.33324 -0.12769 H -4.46366 4.83431 1.94242 H -4.95412 5.55609 -2.26708 H -5.35965 6.23448 0.09225 O -0.00596 0.18909 -0.38848 C 1.37286 -1.18896 1.93555 O 1.23968 -2.29496 2.40992 0 2.51709 -0.78625 1.32758 C 0.58731 0.71591 3.3226 H 1.57947 1.17756 3.31416 H 0.5261 0.05537 4.19266 H-0.15623 1.51021 3.43982 C 3.54601 -1.78463 1.23372 H 3.19296 -2.60846 0.60534 H 3.73181 -2.20117 2.23092 C 4.79815 -1.16575 0.66485 C 5.7404 -1.99618 0.0426 C 5.06526 0.203 0.78819

C 6.9349 -1.47804 -0.44722 H 5.53897 -3.05881 -0.06013 C 6.25206 0.74067 0.29669 H 4.33716 0.84771 1.26561 C 7.17393 -0.10868 -0.31642 H 7.67225 -2.11745 -0.91897 H 6.46959 1.79819 0.39477 S 8.69004 0.56657 -0.94376 O 9.6907 -0.47804 -1.06337 O 8.96709 1.84553 -0.31613 F 8.23348 0.9125 -2.46356



B-Int4

B3LYP/6-31G(d,p) optimized $\Delta G_{gas}(B3LYP) = -2312.914641 a.u.$ Zero-point energy correction = 0.522877 a.u. SMD(THF)B3LYP-D3/6-311++G(d,p) calculated single-point energies: HF = -2314.159383 a.u. C 3.25711 1.28744 -0.52389 N 3.73082 2.47744 -1.0297 N 4.00835 0.37137 0.03388 N 1.91152 1.07867 -0.58091 C 2.86616 3.52614 -1.5662 H 2.90375 3.50641 -2.66724 H 3.27621 4.49491 -1.2531 C 5.16412 2.7061 -1.19886 H 5.32581 3.14562 -2.19217 H 5.50476 3.44852 -0.46159 C 0.98544 1.93774 -1.28577 H 0.94021 1.69841 -2.36102 H-0.0107 1.78298 -0.86934

C 5.42879 0.65152 0.16463

H 5.95454 -0.30137 0.28198 H 5.63317 1.2378 1.07602 C 1.42524 3.38253 -1.09283 H 0.77867 4.06678 -1.64756 H 1.34564 3.63869 -0.03163 C 5.95436 1.41108 -1.05246 H 5.81698 0.78924 -1.94382 H 7.02095 1.63949 -0.96138 H 3.59867 -1.13249 0.36535 H 1.58885 0.19883 -0.18667 O 1.21946 -1.26309 0.90519 C 1.44425 -0.86328 2.26921 H 2.39972 -0.33431 2.3341 H 1.49661 -1.75621 2.90009 0 1.83126 -2.38434 -0.94797 C 2.08587 -2.32323 0.43506 03.375 -2.0949 0.67231 C 0.46255 -2.60515 -1.26945 H 0.41708 -2.71796 -2.35369 C-0.07251 -3.87696 -0.56786 C 0.35548 -3.84321 0.92058 H 0.21606 -4.8225 1.38013 H-0.25732 -3.1189 1.46657 H-0.13307 -1.73208 -0.99015 C 0.29663 0.02664 2.66586 C 0.35242 1.40415 2.41944 C-0.86015 -0.51014 3.24388 C-0.72401 2.22993 2.7451 H 1.2404 1.82132 1.95553 C -1.93832 0.31256 3.5736 H-0.91077 -1.5775 3.44238 C-1.87244 1.68505 3.32374 H -0.67677 3.29128 2.52753 H-2.82923 -0.117 4.02123 H-2.71572 2.3251 3.56118 O 1.73412 -3.52569 1.06511 C 0.47541 -5.13881 -1.25605 H 0.18128 -5.17016 -2.30911

H 0.10909 -6.04342 -0.76228 H 1.56582 -5.12165 -1.19618 C-1.59055 -3.86067 -0.58143 0-2.27155 -3.32456 -1.42907 O -2.10951 -4.58987 0.4437 C-3.47136 -5.04205 0.28807 H -3.92959 -4.99672 1.277 H-3.99394 -4.36219 -0.38964 C-3.45299 -6.45814 -0.24246 C-2.67227 -6.77559 -1.36494 C-4.17816 -7.46944 0.39351 C-2.57971 -8.08264 -1.82232 H-2.12357 -6.00494 -1.89149 C-4.13151 -8.78276 -0.07262 H-4.77834 -7.23493 1.26738 C-3.31941 -9.07036 -1.1678 H-1.95203 -8.3254 -2.66888 H-4.69273 -9.5741 0.40955 S-3.20619 -10.74646 -1.72459 0-1.82832 -11.10307 -2.01921 O -4.06523 -11.60229 -0.92795 F-3.92455 -10.59738 -3.17388



B-Int5

B3LYP/6-31G(d,p) optimized $\Delta G_{gas}(B3LYP) = -2312.916720 a.u.$ Zero-point energy correction = 0.521177 a.u. SMD(THF)B3LYP-D3/6-311++G(d,p) calculated single-point energies: HF = -2314.1562322 a.u. C -4.66111 -2.53802 -0.35967 N -5.18424 -3.81013 -0.45294 N -4.05477 -1.91007 -1.33222 N -4.819 -1.87607 0.83244

C -5.8664 -4.48953 0.6474 H -5.18917 -5.23042 1.10334 H -6.71212 -5.05076 0.22954 C -4.96582 -4.61756 -1.65458 H -4.76656 -5.64954 -1.33785 H -5.88572 -4.64035 -2.25858 C -5.23486 -2.53955 2.05208 H -4.40723 -3.08444 2.53853 H -5.57852 -1.77701 2.75728 C -3.94915 -2.56554 -2.62576 H -3.08669 -2.14305 -3.15191 H -4.83239 -2.34351 -3.24747 C -6.35918 -3.51135 1.70925 H -6.68198 -4.06676 2.5952 H -7.21736 -2.94615 1.33075 C -3.80008 -4.07995 -2.47951 H -2.85492 -4.30159 -1.97035 H -3.77837 -4.57839 -3.45422 H -3.78994 -0.32525 -1.22195 H -4.27558 -1.02065 0.90592 0 -2.51356 2.36372 -0.12975 C -2.49737 3.16162 -1.32074 H -3.41117 2.95888 -1.89175 H -1.64524 2.88145 -1.95252 O -2.79634 0.3998 0.94185 C -2.64381 0.98789 -0.34609 O -3.70972 0.6942 -1.09792 C -1.66916 0.53083 1.81148 H -1.92379 -0.00348 2.72919 C -0.41318 -0.0658 1.14573 C -0.27505 0.62922 -0.22891 H 0.522 0.17775 -0.82305 H -0.04846 1.69486 -0.08992 H -1.50751 1.58451 2.05968 C -2.41608 4.61808 -0.9329 C -1.68171 5.51382 -1.71765 C -3.10651 5.1052 0.18404 C -1.64429 6.87308 -1.40238

H -1.13347 5.14509 -2.58146 C -3.06211 6.46124 0.50569 H -3.66595 4.41001 0.80106 C -2.33408 7.35071 -0.28781 H -1.06915 7.55538 -2.02201 H -3.59847 6.8255 1.37757 H -2.30172 8.40697 -0.03644 O -1.47365 0.46904 -0.97955 C -0.55332 -1.59284 0.96334 H -0.69576 -2.08947 1.92885 H 0.3386 -2.01134 0.48829 H -1.41637 -1.80104 0.32789 C 0.78763 0.22809 2.02977 0 0.74093 0.58361 3.18755 0 1.96097 0.02406 1.37289 C 3.14919 0.26328 2.1482 H 3.11377 -0.35711 3.05184 H 3.16477 1.30603 2.48008 C 4.36381 -0.06312 1.31609 C 4.31989 -1.0251 0.29928 C 5.57388 0.58519 1.59744 C 5.4662 -1.34356 -0.42423 H 3.38093 -1.51318 0.06601 C 6.73086 0.27465 0.88932 H 5.61144 1.34608 2.3719 C 6.66133 -0.69292 -0.1144 H 5.43775 -2.0752 -1.22373 H 7.66646 0.78304 1.09255 S 8.12863 -1.09439 -1.02933 0 9.08638 -0.00792 -0.93956 07.77761 -1.72758 -2.28692 F 8.72085 -2.28027 -0.08996



B-TS4

B3LYP/6-31G(d,p) optimized $\Delta G_{gas}(B3LYP) = -2312.909390 a.u.$ Zero-point energy correction = 0.520067 a.u. SMD(THF)B3LYP-D3/6-311++G(d,p)calculated single-point energies: HF = -2314.1565057 a.u. C 2.48965 3.54556 0.34316 N 2.23511 4.86808 0.56606 N 3.4135 3.17442 -0.55266 N 1.81766 2.59712 0.99979 C 1.28976 5.30723 1.59678 H 0.32999 5.5756 1.13084 H 1.69423 6.21881 2.05135 C 2.90766 5.92778 -0.19233 H 2.17676 6.72572 -0.36726 H 3.7186 6.35823 0.4139 C 0.77993 2.90422 1.97025 H -0.20861 2.95178 1.488 H 0.74665 2.08329 2.69212 C 4.24659 4.12953 -1.26428 H 4.5607 3.66248 -2.20134 H 5.15916 4.35916 -0.69344 C 1.08721 4.23022 2.65777 H 0.27161 4.5211 3.32616 H 1.99652 4.1281 3.25999 C 3.45217 5.40562 -1.5184 H 2.62335 5.19013 -2.2015 H 4.08106 6.17051 -1.98303 H 3.72086 2.16179 -0.56208

H 1.95074 1.55966 0.71753 0 3.80607 -1.53291 -0.41294 C 4.4617 -1.68965 0.84943 H 3.80868 -1.29747 1.63696 H 5.37682 -1.08541 0.84637 0 2.07602 0.08555 0.35815 C 3.54575 -0.22555 -0.75231 O 4.33464 0.68792 -0.45187 C 0.9771 -0.71677 0.07705 H 0.09481 -0.3991 0.65746 C 0.60853 -0.67637 -1.4475 C 1.86486 -1.07448 -2.24735 H 1.6805 -1.0045 -3.32256 H 2.15919 -2.09922 -2.0138 H 1.17796 -1.76935 0.34613 C 4.77534 -3.14862 1.07138 C 4.77743 -3.67049 2.37003 C 5.1175 -3.98999 0.00547 C 5.12423 -5.00182 2.60385 H 4.50248 -3.02963 3.20452 C 5.45469 -5.32343 0.23638 H 5.10485 -3.59304 -1.00407 C 5.46313 -5.83373 1.53613 H 5.11988 -5.39072 3.61838 H 5.71215 -5.96595 -0.60116 H 5.72678 -6.87233 1.71452 0 2.94254 -0.16701 -1.98756 C 0.13291 0.73288 -1.84645 H -0.72721 1.0417 -1.24601 H -0.15123 0.77463 -2.90398 H 0.94852 1.43917 -1.6852 C -0.46828 -1.70953 -1.71814 0 -0.34271 -2.72382 -2.37157 0 -1.64299 -1.38901 -1.0991 C -2.70598 -2.33985 -1.26496 H -2.77829 -2.61566 -2.32353 H -2.46901 -3.25651 -0.71451 C -3.99491 -1.72995 -0.7745

Supporting Information

C -4.23836 -0.35548 -0.89647
C -4.98862 -2.55749 -0.23558
C -5.45073 0.18922 -0.48422
H -3.46867 0.28548 -1.31051
C -6.21014 -2.03172 0.17602
H -4.80686 -3.62383 -0.13565

C -6.42337 -0.65819 0.05014

H -5.65092 1.25009 -0.58349
H -6.98631 -2.66877 0.58455
S -7.9677 0.02962 0.58736
O -8.18829 1.31938 -0.04093
O -8.98776 -1.00159 0.63492
F -7.60123 0.35554 2.13706

Supporting Information

Schemes

substitution:









Scheme S3. ROP of FMC with varieties of alcohols as the initiator and TBD as the organocatalyst: a) 1-pyrenemethanol; b) polyethylene glycol monomethyl ether (mPEG).



Scheme S4. Copolymerization with δ -valerolactone (VL): a) p(FMC-*r*-VL) from random copolymerization (simultaneous feeding); b) p(FMC-*b*-VL) from block copolymerization (sequential feeding).



Scheme S5. The general ptocedure for polymerisation postmodification of pFMC *via* SuFEx click reaction with silyl ether-protected functional modules.



Scheme S6. The experimental synthesis scheme of functional pFMCs: a) reaction with TBDMS-IL to prepare pFMC-IL for antimicrobial properties; b) reaction with TBDMS-mPEG to prepare pFMC-mPEG for micelles/vesicles; c) reaction with bisTBDMS-PEG as the crosslinker to yield crosslinked pFMC-PEG for hydrogels.



Scheme S7. Validation scheme of TBD as a co-organocatalyst for modification *via* a stepwise strategy. pFMC is modified through the SuFEx click reaction with silyl ether-protected functional modules: a) TBDMS-HDFD; b) TBDMS-DR1; c) TBDMS-TPE.



Scheme S8. Validation scheme of TBD as a co-organocatalyst for modification *via* a one-pot strategy. The one-pot procedures are adopted using FMC, benzyl alcohol, TBD, as well as silyl ether-protected functional modules: a) TBDMS-HDFD; b) TBDMS-DR1; c) TBDMS-TPE.

Figures



Figure S1. ¹H NMR spectrum of MCC in CD₃OD.



Figure S2. ¹⁹F NMR spectrum of FMC in CDCl₃.



Figure S3. MS of FMC in MeCN: m/z calcd for $C_{13}H_{13}FO_7S+Na^+$: 355.0253 [*M*+Na]+; found: 355.0258.



Figure S4. FT-IR spectrum of FMC and pFMC via the KBr compression method.



b)



Figure S5. a) MALDI-TOF MS spectrum of medium-molecular-weight pFMC and b) a larger version

Supporting Information



Figure S6. ¹H NMR spectra of a) 1-pyrenyl methanol-initiated pFMC and b) mPEG-initiated pFMC in $CDCl_3$.



Figure S7. a) Photographs of samples under natural light (left) and a black light at a wavelength of 365 nm (right), NMR tubes from left to right: 1-pyrenylmethanol, Py-pFMC, Bn-pFMC, and mPEG-pFMC, respectively dissolved in CDCl₃ at a concentration of 1 mg/mL; b) UV–vis absorption spectrum and c) PL spectrum (λ_{ex} =340 nm, 298K) of samples dissolved in acetonitrile at the mass concentrations of 1 mg/L, in which FMC is taken as the control group.



Figure S8. ¹H NMR spectra in CDCl₃: a) p(FMC-*r*-VL), and b) p(FMC-*b*-VL).



Figure S9. Thermal properties characterization: a) TG-DTG thermograms of pFMC, PVL, p(FMC*r*-VL), and p(FMC-*b*-VL) (i) TG and (ii) DTG; b) baseline extrapolation of DSC curves to measure the T_q of pFMC, p(FMC-*r*-VL), and p(FMC-*b*-VL).



Figure S10. ROP Kinetics of FMC: a) ¹H NMR, b) contrast of characteristic peaks on ¹H NMR, and c) GPC elution curves at the stipulated polymerisation time (NMR in CDCl₃, GPC in DMF).





Figure S11. The chain extension experiment: a) number average molecular weight measured by GPC *M*(*n*, *GPC*) (blue squares) and *PDI* (while diamond) as a function of time; b) ¹H NMR, and c) GPC elution curves at the end of each cycle (NMR in $CDCI_3$, GPC in DMF).



Figure S12. DFT computed Gibbs free energy profile diagram for the nucleophilic catalytic mechanism (Mechanism A) and the acid-base catalytic mechanism (Mechanism B) at the level of SMD(THF)-B3LYP-D3/6-311++G(d,p).



Figure S13. Mass change curves of pFMC as a function of time. Each point contains the mean \pm SD of three independent experiments.



Figure S14. OD values of PS well plates and pFMC coatings at different proliferation times. Error bars represent the standard deviation of the mean (n = 3). **, and ***, respectively indicate P < 0.05, and P < 0.01 (calculated by student's t test). In addition, the stars on the error bars of pFMC coatings were calculated by comparing data from pFMC coatings and PS well plates at the same incubation time.



b)





Supporting Information



Figure S16. Characterization of pFMC-mPEG: a) ¹H NMR spectrum in CDCl₃, b) GPC report in DMF.

w

100000

10000

100



Figure S17. The fiber diameter distribution of the fibers with a) gelatin, b) gelatin-pFMC blend, where the data are presented as the mean \pm SD (n = 30).



Figure S18. ¹H NMR spectra in CDCl₃: a) pFMC-DR1 from the stepwise strategy; b) pFMC-DR1 from the one-pot strategy.



Figure S19. ¹H NMR spectra in $CDCl_3$: a) pFMC-TPE from the stepwise strategy; b) pFMC-TPE from the one-pot strategy.



Figure S20. Photographs of samples tape-casting on silicon wafers under different light conditions: a) under natural light; b) under a black light at a wavelength of 365 nm. c) Photographs used to demonstrate the AIE phenomenon, where the samples were dissolved in different solvents under a black light at a wavelength of 365 nm, each tube from left to right: TBDMS-TPE, pFMC, pFMC-TPE stepwise, pFMC-TPE one-pot (mass concentration: 10 mg/mL).

Tables

Initiators	NMR		GPC	
	DP	<i>M_n</i> / kDa	<i>M_n</i> / kDa	PDI
BnOH	18	6.1	6.5	1.18
РуОН	NA ^[a]	NA ^[a]	6.9	1.21
mPEG	19	8.3	8.6	1.30

Table S1. Molecular weight of pFMCs initiated by different primary alcohols

[a] Not Applicable. In the ¹H NMR analysis, the characteristic peaks of 1-pyrenyl methanol at the end of the chain was obscured by those of pFMCs, and thus no specific *DP* or M_n data could be obtained.

Table S2. Molecular weight of pFMC at the given polymerization time.

Polymerisation Time	NN	/IR	GP	С
	Conv. / %	<i>M_n</i> / kDa	<i>M_n</i> / kDa	PDI
30s	58.55%	3.9	4.4	1.40
1 min	59.61%	4.0	5.1	1.48
2 min	66.90%	4.4	5.2	1.43
5 min	66.99%	4.4	5.3	1.43
15 min	66.80%	4.4	5.2	1.45

Table S3. Molecular weight of pFMC at the end of each chain extension cycle.

Cycles	NN	ИR	GF	PC .
	DP	<i>M_n</i> / kDa	<i>M_n</i> / kDa	PDI
(1)	18	6.1	6.9	1.21
(2)	35	11.7	12.1	1.26
(3)	~ 50 ^[a]	~ 16.7 ^[a]	18.7	1.30

[a] An estimated value. It is because as the degree of polymerization increases, the proportion of end groups in the whole becomes smaller, resulting in an increased difficulty and decreased accuracy in the calculation of DP or M_n .

Table S4. Surface element analysis data for electrospun membranes.	

Components	EDS element analysis (wt%)				
	[C]	[N]	[0]	[S]	[F]
Gelatin	52.89	22.64	24.37	0.10	_ [a]
Gelatin-pFMC blend	54.27	19.89	25.15	0.32	0.37

[a] No data. EDS did not detect the presence of this element on the sample.

Abbreviations

AIE: aggregation-induced emission; APC: aliphatic polycarbonate; a.u.: arbitrary unit; bisTBDMS-PEG: polyethylene glycol bis(tert-butyl dimethylsilane) ether; BnOH: benzyl alcohol; CCK-8: Cell Counting Kit 8; CD₃OD: methanol- d_4 ; CDCl₃: chloroform-d; CDI: 1,1'-carbonyldiimidazole; CL: ε caprolactone; CuAAC: copper(I)-catalyzed azide-alkyne cycloaddition; Da: Dalton; DBU: 1,8diazabicyclo[5.4.0]undec-7-ene; DCM: dichloromethane; DCTB: trans-2-[3-(4-tertButylphenyl)-2methyl-2-propenylidene]malononitrile; DFT: density functional theory; DLS: dynamic light scattering; DMF: N,N-dimethylformamide; DMPA: 2,2-bis(hydroxymethyl)propionic acid; DP: degree of polymerization; DR1: disperse red 1; DSC: differential scanning calorimetry; E. coli: Escherichia coli; EDS: energy disperse spectroscopy; FBS: foetal bovine serum; FMC: 4'-(Fluorosulfonyl)benzyl 5-methyl-2-oxo-1,3-dioxane-5-carboxylate; f_w : water fractions; GPC: gel permeation chromatography; HDFD: 1H,1H,2H,2H-heptadefluoro-1-decanol; IL: ionic liquid; KHF₂: potassium hydrogen fluoride; LLA: (L)-lactide; MALDI-TOF MS: matrix-assisted laser desorption ionization time-of-flight mass spectrometry; MCC: 5-methyl-5-carboxyl-1,3-dioxan-2one; MeCN: acetonitrile; MeOH: methanol; M_{n, GPC}: number-average molecular weight measured by GPC analysis; $M_{n, NMR}$: number-average molecular weight measured by NMR analysis; mPEG: poly(ethylene glycol) monomethyl ether; mPEG-pFMC: pFMC initiated by mPEG; MS: mass spectrometry; NMR: nuclear magnetic resonance; OD: optical density; PBS: phosphate buffered saline; PDI: polymer dispersity index; PEG: poly(ethylene glycol); pFMC: poly(4'-(Fluorosulfonyl)benzyl 5-methyl-2-oxo-1,3-dioxane-5-carboxylate); PPM: post-polymerization modification; PyOH: 1-pyrenyl methanol; Py-pFMC: pFMC initiated by 1-pyrenyl methanol; ROP: ring-opening polymerization; SEM: scanning electron microscope; SuFEx: sulfur(VI)-fluoride exchange; TBD: 1,5,7-triazabicyclo[4,4,0]dec-5-ene; TBDMS-CI: *tert*- butyldimethylchlorosilane; TBDMS-DR1: N-(2-((tert-butyldimethylsilyl)oxy)ethyl)-N-ethyl-4-((4-nitrophenyl)diazenyl)aniline; **TBDMS-HDFD:** tert-butyl((3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10) heptadecafluorodecyl)oxy)dimethylsilane; TBDMS-IL: 1-(6-((tert-butyldimethylsilyl)oxy)hexyl)-3methyl-1H-imidazol-3-ium TBDMS-mPEG: *tert*-butyl(2-methoxy bromide; polyethoxy)dimethylsilane; TBDMS-TPE: tert-butyldimethyl((4-(1,2,2triphenylvinyl)benzyl)oxy)silane; TEA: triethylamine; TEM: transmission electron microscope; TFE: 2,2,2-trifluoroethanol; TGA: thermal gravimetric analyses; THF: tetrahydrofuran; TMC: trimethylene carbonate; TPE: tetraphenylene; TPE-OH: (4-(1,2,2triphenylvinyl)phenyl)methanol; VL: δ -valerolactone.

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