Supplementary Information for b000000x

Initiator-lightened Polymers : preparation of end-functionalized polymers by ATRP and their intramolecular charge transfer and aggregation-induced emission

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General Information

CuBr (Sinopharm Chemical Reagent Co., Ltd, 98.5%) was purified in acetic acid, washed with methanol and dried under vacuum to afford a white powder. Cyclohexanone and N,N,N',N",N",Pentamethyldiethylenetriamine (PMDETA) were distilled under vacuum. 4'-Hydroxyacetophenone (TCI) and 4-Dimethylaminobenzaldehyde (TCI) were used as received without further purification. All other reagents and solvents were analytic pure and were used as received without further purification.

¹ H NMR spectra were measured by INOVA 300 MHz NMR spectrometer and ¹³C NMR spectra were measured by INOVA 400 MHz NMR spectrometer, *CDCl*₃ or *DMSO-d*₆ as solvent and tetramethylsilane (TMS) as the internal standard at ambient temperature. Molecular weights and the polydispersity relative to PS were measured using Waters1515 GPC with THF as a mobile phase at a flow rate of 1 mL/min and with column temperature of 30 °C. UV-vis absorption spectra were determined on a Shimadzu RF540 spectrophotometer. Room temperature emission and excitation spectra were carried out using Edinburgh-920 fluorescence spectra photometer and fluorescence lifetimes were measured with Fluorolog®-3 spectrometer. The fluorescent quantum yield (QY) in the solution and aggregate states were determined by using fluorescein ($\Phi_F = 79$ % in 0.1 M NaOH as standard), whereas that of solid film was measured using a calibrated integrating sphere.

Preparation of Nanoaggregates

Stock solutions of the PS in DMF with a concentration of 5 mM were prepared. Aliquots (1 mL) of the stock solutions were transferred to 10 mL volumetric flasks. After adding appropriate amounts of DMF, ethanol was added dropwise under vigorous stirring to furnish 5 μ M solutions with defined fractions of water (f_e = 0 – 99 vol %). Spectral measurements of the resultant solutions or aggregate suspensions were performed immediately.

S1. Initiator

S1-1. Synthesis of Initiator (TPP-NI)

3 and 4 were prepared according to the relevant published literature^{1a, 1b}. 2 was synthesized by reacting 4 with chalcone 3, as follows. A mixture of 4 (10 mmol) and chalcone 3 (10 mmol) in ethanol (50 mL), and 37 % HCl (5 mL), was refluxed for 24 hr. The resulting mixture was cooled, and the precipitate filtered to afford the crude products, which were recrystallized from ethanol. 1 was synthesized by reacting 2 with 2-bromopropionyl bromide, as follows. A mixture of 2 (1.0 mmol) and triethylamine (3.0 mmol) in THF (100 mL) was cooled to 0 °C in an ice/water bath. Then, 2-bromopropionyl bromide (2.0 mmol) in THF (40 mL) was added to a 50 mL pressure equalizing addition funnel fitted to the flask under N₂(g). After being added dropwise, the reaction mixture was stirring overnight and allowed to warm to room temperature. The solution was then filtered and poured into a large amount of water; the precipitate was filtered to afford the crude products, which were recrystallized from ethanol.



Scheme 1. Synthetic routines for initiator and its polymers. For PSa = 30,920 g/mol; PSb = 19,800 g/mol; and PSc = 10,050 g/mol.

2-butyl-6-hydrazinyl-1H-benzo[de]isoquinoline-1,3-(2H)-dione (4) Yield : 78 % ¹H NMR (300 MHz, *DMSO-d*₆) δ 9.12 (s, 1H), 8.60 (d, *J* = 8.3 Hz, 1H), 8.41 (d, *J* = 7.2 Hz, 1H), 8.28 (d, *J* = 8.6 Hz, 1H), 7.63 (t, *J* = 7.9 Hz, 1H), 7.24 (d, *J* = 8.6 Hz, 1H), 4.67 (s, 2H), 4.10 – 3.94 (m, 2H), 1.58 (dt, *J* = 14.9, 7.4 Hz, 2H), 1.33 (dq, *J* = 14.6, 7.4 Hz, 2H), 0.91 (t, *J* = 7.3 Hz, 3H).

3-(4-(dimethylamino)phenyl)-1-(4-hydroxyphenyl)prop-2-en-one (3) Yield : 70 % ¹H NMR (300 MHz, *DMSO-d*₆) δ 10.30 (s, 1H), 8.02 (d, *J* = 8.5 Hz, 2H), 7.68 (d, *J* = 8.7 Hz, 2H), 7.61 (s, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 6.74 (d, *J* = 8.5 Hz, 2H), 3.00 (s, 6H).

2-butyl-6-(5-(4-(dimethylamino)phenyl)-3-(4-hydroxyphenyl)-4,5-dihydro-1H-pyrazo l-1-yl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (2)

Yield : 83 %, red powder, bp : 171 \pm 1 °C,LC-MASS : 533.2534 (M⁺, calcd,

533.2547)

¹H NMR (300 MHz, *DMSO-d*₆) δ 9.79 (s, 1H), 9.764 (d, 1H), 8.48 (d, *J* = 7.2 Hz, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 7.80 (t, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 3.6 Hz, 2H), 7.06 (s, 2H), 6.91 (t, *J* = 9.5 Hz, 3H), 5.96 – 5.86 (m, 1H), 4.01 – 3.89 (m, 3H), 3.20 (d, *J* = 19.9, 6.1 Hz, 1H), 2.91 (s, 6H), 1.64 – 1.48 (m, 2H), 1.40 – 1.23 (m, 2H), 0.90 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (400 MHz, *DMSO-d₆*) δ 163.57, 162.64, 159.49, 153.42, 145.18, 134.40,
131.95, 130.78, 130.04, 128.29, 127.43, 124.65, 122.19, 121.62, 115.76, 111.73,
110.06, 63.93, 43.81, 41.93, 29.68, 19.79, 13.71.

4-(1-(2-butyl-1,3-dioxo-2,3-dihydro-1H-benzo[de]isoquinoline-6-yl)-5-(4-(dimethyla mino)phenyl) -4,5-dihydro-1H-pyrazol-3-yl)phenyl 2-bromo-2-methylpropanoate (1)

Yield : 86 %, orange powder, bp : 163 ± 1 °C, LC-MASS : 681.2072 (M⁺, calcd, 681.2071)

¹H NMR (300 MHz, *DMSO-d*₆) δ 9.63 (d, *J* = 8.5 Hz, 1H), 8.49 (d, *J* = 7.2 Hz, 1H), 8.19 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.5 Hz, 2H), 7.81 (t, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.5 Hz, 2H), 7.19 (d, *J* = 8.5 Hz, 2H), 7.07 (d, *J* = 8.6 Hz, 1H), 6.63 (d, *J* = 8.5 Hz, 2H), 5.93 (d, *J* = 7.2 Hz, 1H), 4.02 – 3.93 (m, 3H), 3.25 (d, *J* = 6.6 Hz, 1H), 2.80 (s, 6H), 2.07 (s, 6H), 1.64 – 1.48 (m, 2H), 1.40 – 1.23 (m, 2H) 0.90 (t, *J* = 7.3 Hz, 3H). ¹³C NMR (400 MHz, *CDCl*₃) δ 170.21, 164.85, 164.05, 151.82, 151.01, 150.32, 145.88, 134.29, 132.46, 131.30, 130.72, 130.18, 127.48, 126.92, 124.74, 123.59, 122.57, 121.73, 114.01, 113.00, 111.18, 66.11, 55.39, 42.58, 40.55, 40.13, 30.74, 30.40, 20.56, 14.03.

S1-2. DFT calculation of TPP-NI molecule

To elucidate the effect of the naphthalimide group on the aggregation-induced fluorescence, the ground-state geometry of the initiator was optimized via hybrid density functional theory (B3LYP) with the 6-31G* basis set in the Gaussian 03 program package. The naphthalimide ring in the 1-position of the pyrazoline ring enjoys the largest conformational flexibility among the three aryl substituents, with the dihedral angle of 58°; the phenyl ring in the 3-position and 5-position of the pyrazoline ring possesses the dihedral angles of 3° and 39°, respectively. As a result, the whole molecule takes a non-planar configuration; this helps to impede the π - π stacking interaction to some extent in an aggregate state, or at the film state.

S2. General procedure for polymerizations

S2-1. Synthesis of PS and PMMA

Initiator, CuBr, PMDETA, monomer (St or MMA), and cyclohexanone were mixed in a round-bottomed flask. The flask was then sealed and cycled three times between vacuum and N_2 conditions. The polymerization was processed at a pre-determined temperature under N_2 . Samples were taken out at different time intervals using a syringe, and were then diluted with tetrahydrofuran (THF). The diluted solution was passed through an alumina column to remove the copper catalyst, and the filtrate was precipitated by the addition of methanol. The precipitation was then filtrated and dried under vacuum.

S2-2. Synthesis of PHEMA

Initiator, CuBr, 2,2'-bpy, HEMA, and cyclohexanone were mixed in a round-bottomed flask. The flask was then sealed and cycled three times between vacuum and N_2 conditions. The polymerization was processed at a pre-determined temperature under N_2 . Samples were then taken out with a syringe at different time intervals, and diluted with DMF. The diluted solution was then passed through an alumina column to remove the copper catalyst, and the filtrate was precipitated by the addition of diethyl ether. The precipitation was then filtrated and dried under vacuum.

Polymerizations of St were carried out with a monomer/initiator molar ratio of 2,000, and the results have been presented in Fig. S2-1 and S2-2. According to Fig. S2-1, the linearity of the semilogarithmic plot of $\ln([M]_0/[M])$ versus the polymerization time indicates that the polymerization is first-order with respect to the monomer. The number average molecular weights (Mn) increased linearly with the conversion, and the PDIs remained relatively narrow in all cases (Mw/Mn = 1.10-1.20); this indicated that the polymerization was well-controlled (Fig. S2-2). The $M_{n(GPC)}$ s were the same as the corresponding $M_{n(th)}$ s, in which the $M_{n(th)}$ s was calculated according to $M_{n(th)} = M_{w, initiator} + ([St]_0 / [initiator]_0) \times M_{w, St} \times Conversion$ ($M_{w, initiator}$ and $M_{w, St}$ were the total molecular weight of initiator, respectively). The GPC chromatograms (Fig. S2-3) displayed narrow, single peaks, and demonstrated that there were no low molecular weight trails indicative of transfer processes.



Figure S2-1. Kinetic plot for the ATRP of St initiated by Initiator TPP-NI in Cyclohexanone solution ($[St]_0$: $[Initiator]_0$: $[CuBr]_0$: $[PMDETA]_0 = 2000 : 1 : 1 : 2$, $[St]_0 = 5.0 \text{ mol/L}$, 80 °C).



Figure S2-2. Dependence of $M_{n(GPC)}$ (g/mol) and PDI with conversion for the polymerization of St initiated by Initiator in Cyclohexanone solution ([St]₀ : [Initiator]₀: [CuBr]₀: [PMDETA]₀ = 2000 : 1 : 1 : 2, [St]₀ = 5.0 mol/L, 80 °C).



Figure S2-3. The GPC traces of the PSt. (a) $M_{n(GPC)} = 2,380$ g/mol, PDI = 1.09; (b) $M_{n(GPC)} = 5,860$ g/mol, PDI = 1.12; (c) $M_{n(GPC)} = 8,580$ g/mol, PDI = 1.13; (d) $M_{n(GPC)}$ = 11,320 g/mol, PDI = 1.14; (e) $M_{n(GPC)} = 14,240$ g/mol, PDI = 1.15; (f) $M_{n(GPC)} = 17,380$ g/mol, PDI = 1.15; (g) $M_{n(GPC)} = 20,260$ g/mol, PDI = 1.17.





Figure S2-4. ¹H NMR spectra of initiator (*CDCl₃*) and polymer (*DMSO-d6*) at r.m.





Figure S2-5. ¹³C NMR spectra of compond 2 ($DMSO-d_6$) and 1 ($CDCl_3$) at r.m.

Figure S2-4 illustrates the ¹H NMR spectra of the polymer, in which the signals of hydrogen atom from the vinyl group (5.5-6.0 ppm) had disappeared, and a broad signal of methylene below 2.0 ppm was formed. Further, the protons of the aromatic rings resonate at $\delta \sim 7.3$ - 10.0 ppm, and the protons of the pyrazoline rings resonate at $\delta \sim 3.0$ - 6.0 ppm, thus confirming that the initiator had indeed been incorporated at the α -end of the polymer chain.



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Figure S2-7LC-MASS compond 2

S3. Thermal stability of initiator and PS

The thermal properties of the initiator and its polymers were investigated by TGA and DSC analyses. As shown in Fig. S3-1, polymers enjoyed higher thermal stability with T_d 's of 370 °C than did initiators with T_d 's of 200 °C. DSC analyses of polymers showed a glass transition temperature (T_g) of 110 °C; the Tg of the initiator was not observed, likely because of its low molecular weight.





Figure S3-1. TGA (top) and DSC (bottom) thermograms of initiator and its polymers, recorded under N_2 at a heating rate of 20 and 10 °C /min, respectively.

S4. Absorption and emission spectra of TPP-NI, PS, PMMA, and PHEMA

The absorption spectra of the initiators have been shown in Fig. S4-1. With the water content increase from pure DMF to a DMF/water ratio of 60 %, the maximum absorption bands were red shifted from 475 nm to 492 nm; the bands were then blue shifted when the water content was gradually increased. The shifts could likely be attributed to different conformations and packing modes upon aggregation, corresponding to different water contents of the molecules.^{2a, 2b} (see S7-1).





Figure S4-1. UV - Vis absorption spectra (top) of TPP-NI showing the variation of absorbance with proportions of water and DMF as indicated; PL spectra (bottom) of TPP-NI in DMF/water mixtures with different water fractions. TPP-NI concentration: 25 uM; excitation wavelength: 467 nm.



Figure S4-2. Absorption (left) and emission (right) of PSa in different solvents. Concentration: 5 uM; excitation wavelength: 467 nm.



Figure S4-3. Absorption (top) and emission (bottom) of PSa in DMF/ethanol mixture. Polymer concentration: 5 uM; excitation wavelength: 467 nm.





Figure S4-4. Absorption (top) and emission (bottom) of PSb in DMF/ethanol mixture. Polymer concentration: 5 uM; excitation wavelength: 467 nm.



Figure S4-5. Absorption (top) and emission (bottom) of PSc in DMF/ethanol mixture. Polymer concentration: 5 uM; excitation wavelength: 467 nm.



Figure S4-6. Change in the relative PL intensity (I/I_0) of PS in the DMF/ethanol mixture. $I_0 = PL$ intensity in pure DMF solution. Concentration: 5 uM; excitation wavelength: 467 nm.



Figure S4-7. Emission spectra of PMMA in the DMF/water mixture. Concentration: 25 uM; excitation wavelength: 467 nm.



Figure S4-8. Absorption and emission spectra of initiator and polymer films.



Figure S4-9. Emission spectra of PHEMA in DMF/water mixture. Polymer concentration: 100 uM; excitation wavelength: 467 nm.



Figure S4-10. Emission spectra of PSa (left) and PMMA (right) in DMF / H_2SO_4 mixture at different pH values. Polymer concentration: 5 uM; excitation wavelength: 467 nm.

S-5. Fluorescence lifetime of initiator and PS

The fluorescence lifetimes of the initiator and the PSa in different solutions were also studied, as shown in Fig. S5-1. Biexponential decay of the initiator and of PSa in Toluene and THF was observed; triexponential decay of the initiator and of PSa in DMF was observed. The lifetime values of the initiator and PSa were collected and have been displayed in Table S5-1.



Figure S5-1. Typical fluorescence decay curves associated with lamp profile for initiator (top) and PSa (bottom) in ambient environment. Excitation wavelength is constant at 300 nm.

Table S5-1. Fluorescence decays of excited states of the initiator and PS in different solvents.

Solvent	Initiator				PSa			
	$A_1/A_2/A_3$	τ_1	τ_2	τ_3	$A_{1}/A_{2}/A_{3}$	τ_1	τ_2	τ_3
		(ns)	(ns)	(ns)		(ns)	(ns)	(ns)
Toluene	0.05/0.95/0	0.93	2.86	0	0.06/0.94/0	0.92	3.01	0
THF	0.95/0.05/0	0.96	2.15	0	0.91/0.09/0	0.90	2.18	0
DMF	0.15/0.76/0.09	3.02	0.21	11	0.78/0.17/0.05	0.29	1.86	7.99

S6. DFT calculation of TPP-NI molecule

To determine the effect of the naphthalimide group on the aggregation-induced fluorescence, the ground-state geometry of the initiator was optimized via the hybrid density functional theory (B3LYP) with 6-31G* basis set, using the Gaussian 03 program package. Among the three aryl substituents, the naphthalimide ring in the 1-position of the pyrazoline ring enjoys the largest conformational flexibility, with the dihedral angle of 58°. The phenyl ring in the 3-position and 5-position of the pyrazoline ring possesses dihedral angles of 3° and 39°, respectively. As a result, the whole molecule exhibits a non-planar configuration, which, to some extent, helps to impede the π - π stacking interaction both in the aggregate state and at the film state. The spatial distributions of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels of the initiator were calculated, and have been shown in Fig. S6-2. The figure clearly show that HOMO is a π orbital, concentrated on the central dimethylaniline moiety, and that LUMO is of π^* character and is distributed on the pyrazoline ring and naphthalimide ring.



Figure S6-1. Optimized ground-state geometry of the initiator with B3LYP/6-31G* in gas phase.



Figure S6-2. Calculated spatial distributions of the HOMO and LUMO levels of the initiator.

S7. SEM images of initiator and polymers in aggregates



Figure S7-1. SEM images, crystalline of initiator formed in DMF/water mixtures with $f_w = 60 \%$ (left, scale bar is 3 µm), and 80 % (right, scale bar is 2 µm).



 $f_{e} = 50\%$

 $f_{e} = 80\%$



 $f_{e} = 90\%$

 $f_{e} = 99\%$

Figure S7-2. SEM images of PS formed in DMF/ethanol mixtures. Scale bar is 1 µm.

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