Supporting Information

Continuously-tunable fluorescent polypeptides through polymer-assisted assembly strategy

Guodong Liang,*a Feng Ren,a Haiyang Gao,a Qing Wu,a Fangming Zhua and Ben Zhong Tang*b

aPCFM and GDHPPC labs, School of Materials Science and Engineering, School of Chemistry and Chimical Engineering, Sun Yat-sen University, Guangzhou, 510275, China. E-mail: lgdong@mail.sysu.edu.cn

bDepartment of Chemistry, Institute for Advanced Study, Division of Biomedical Engineering and Institute of Molecular Functional Materials, The Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong, China. E-mail: tangbenz@ust.hk

Materials. Ethanediamine, methyl acrylate, L-glutamic acid, benzyl alcohol, pyridine, triphosgene, benzophenone, and aminobenzophenone were purchased from Sigma-Aldrich (China) and used without further purification unless otherwise indicated. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl immediately prior to use.
Synthesis.

Scheme S1. Synthetic route for detrimer amidoamine initiators.

Synthesis of detrimer amidoamine initiator. The synthesis protocol for amidoamine initiator was adapted from previous literature procedures.\(^1\) A typical run was shown as follows. A methanol solution (10 mL) of ethylenediamine (0.6 g, 10 mmol) was added dropwise into a methyl acrylate (5.16 g, 60 mmol) in methanol (20 mL) at 0 °C. The resulting reaction mixture was allowed to warm to room temperature and stirred for 2
days under N₂. Then the volatiles were removed under reduced pressure using a rotary evaporator and then in a vacuum at 40 °C to give 3.8 g product (1) as slightly yellow oil (yield: 94%). \(^1\)H NMR (300 MHz, CDCl₃, 298 K): \(\delta \ 2.42\) (m, 12 H, NCH₂), 2.72 (m, 8H, CH₂COOCH₃), 3.65 (m, 12H, COOCH₃). The \(^1\)H NMR spectrum agreed with the literature data.\(^1\)

A methanol solution (3 mL) of 1 (0.808 g, 2mmol) was added dropwise into a round-bottomed flask containing ethylenediamine (1.202 g, 20mmol) and anhydrous methanol (7 mL) at 0 °C using an ice/water bath. The reaction mixture was allowed to warm to room temperature and stirred for 7 days under N₂ until complete disappearance of terminal methyl ester groups of 2, monitored by \(^1\)H NMR. Then the volatiles were removed using a rotary evaporator to get crude product. To the crude product was added 20 mL anhydrous methanol and then removed the solvent using a rotary evaporator. Repeat this cycle three times to remove un-reacted ethylenediamine, and finally residual volatiles were removed in vacuum at 40 °C overnight to give 0.986 g product (2) as viscous slightly yellow oil (yield: 95%).

**G1**: \(^1\)H NMR (300 MHz, CDCl₃, 298 K): \(\delta \ 2.34–2.44\) (m, 12H, COCH₂ and NCH₂CH₂N), 2.64 (m, 8H, CH₂NH₂), 2.82 (m, 8H, NCH₂CH₂CO), 3.30 (m, 8H, CONHCH₂), 7.95 (br, 4H, CONH). The signal at 3.65 ppm derived from OCH₃ is neglectable. The \(^1\)H NMR spectrum agreed with the literature data.\(^1\)

**G2**: \(^1\)H NMR (300 MHz, CDCl₃, 298 K): \(\delta \ 1.70–1.96\) (m, 16H, CH₃NH₂), 2.28–2.44 (m, 28H, COCH₂ and NCH₂CH₂N), 2.48–2.58 (br, 8H, NCH₂CH₂NH), 2.64-2.78 (m, 16H, CH₂NH₂), 2.80-2.95 (m, 24H, NCH₂CH₂CO), 3.18-3.42 (m, 24H, CONHCH₂),
7.68-8.00 (m, 12H, CONH). The signal at 3.65 ppm derived from OCH₃ is neglectable.

**G3:** ¹H NMR (300 MHz, CDCl₃, 298 K): δ 1.70–1.96 (m, 32H, CH₃NH₂), 2.28–2.44 (m, 60H, COCH₂ and NCH₂CH₂N), 2.48–2.78 (m, 56H, NCH₂CH₂NH and CH₂NH₂), 2.80-2.95 (m, 56H, NCH₂CH₂CO), 3.18-3.42 (m, 56H, CONHCH₂), 7.57, 8.00 (m, 28H, CONH). The signal at 3.65 ppm derived from OCH₃ is neglectable.

**G4:** ¹H NMR (300 MHz, CDCl₃, 298 K): δ 1.70–1.96 (m, 64H, CH₃NH₂), 2.28–2.44 (m, 124H, COCH₂ and NCH₂CH₂N), 2.48–2.58 (br, 56H, NCH₂CH₂NH), 2.64-2.78 (m, 64H, CH₂NH₂), 2.80-2.95 (m, 120H, NCH₂CH₂CO), 3.18-3.42 (m, 120H, CONHCH₂), 7.68-8.10 (m, 60H, CONH). The signal at 3.65 ppm derived from OCH₃ is neglectable.

**Synthesis of γ-Benzyl-L-glutamate carboxyanhydrides (BLG-NCA).**

![Scheme S2](image)

**Scheme S2.** Synthetic route of γ-benzyl-L-glutamate carboxyanhydrides (BLG-NCA).

The preparation for BLG-NCA was adapted from literature procedures.² A typical run was shown as follows. To 100 mL of ethyl ether was slowly added 15 mL of
concentrated sulfuric acid (98%) in an ice-bath. To the solution was slowly added 220 mL of benzyl alcohol. Ethyl ether was removed under reduced pressure at room temperature. The solution was heated to 70 °C. To the solution was added 22 g of L-glutamic acid with stirring. This mixture was held at 70 °C with stirring until all glutamic acid was dissolved (ca. 1.5 hours). The reaction mixture was cooled to 30 – 40 °C, and then added to a solution of 33 mL pyridine in 220 mL 95% ethanol under stirring. Precipitation occurred upon cooling to 20 °C and the precipitation was allowed to continue at 3 °C for 12 h. The precipitate was then collected by filtration, washed with ethanol, then with ethyl ether and air-dried. The product was re-crystallized from 500 mL of 5% ethanol aqueous solution, followed by adding sufficient sodium bicarbonate to keep the pH at 7. After filtration, the solution was cooled as rapidly as possible to 3 °C, and left for 12 h. The precipitate was collected by filtration, washed with water and adjusted to pH 7 with sodium bicarbonate, washed with distilled water, slurried with ethanol, filtered, washed with ethyl ether and air-dried, to yield 16.0 g white plates of γ-benzyl-L-glutamate (yield: 31.1%). ¹H NMR (300 MHz, CDCl₃, 298K): δ 2.41 (m, 2H, COCH₂C₆H₅), 2.84 (t, 2H, COCH₂CH₂), 4.37 (t, 1H, COCHNH₂), 5.18 (s, 2H, COOCH₂Ph), 7.30–7.39 (m, 5H, COOCH₂Ph).

γ-Benzyl-L-glutamate (10 g) was suspended in 150 mL anhydrous THF and then triphosgene (4.5 g) was added under nitrogen. The mixture was stirred at 50 °C under N₂ until it turned into a transparent solution within 3 h. The product was precipitated by pouring the solution into 500 mL hexane, isolated by filtration, and purified by re-
crystallizing three times from the THF/hexane mixed solution. The yield was 49%. \(^1\)H NMR (300 MHz, CDCl\(_3\), 298K): \(\delta\) 2.14 (m, 2H, COCH\(_2\)CH\(_2\)), 2.61 (t, 2H, COCH\(_2\)CH\(_2\)), 4.39 (t, 1H, COCHNH), 5.12 (br, 2H, COOCH\(_2\)Ph), 6.6 (s, 1H, CONH), 7.30–7.38 (m, 5H, COOCH\(_2\)Ph). The \(^1\)H NMR spectrum agreed with the literature data.\(^2\)c

**Synthesis of star poly(\(\gamma\)-benzyl-L-glutamate) (PBLG).**

Prescribed amount of amidoamine initiator (0.035 mmol) and \(\gamma\)-Benzyl-L-glutamate carboxyanhydrides (BLG-NCA) (1.52 mmol) were dissolved in 50 mL anhydrous THF and the solution was stirred for 72 h at room temperature under N\(_2\). The resulting mixture was added dropwise to ethanol. The precipitate was isolated by filtration and dried under vacuum at 40 °C overnight to yield 4-armed poly(\(\gamma\)-benzyl-L-glutamate) as white solids.

**PBLG1 (B\(_{96}\)):** \(^1\)H NMR (300 MHz, CDCl\(_3\)+15 vol% TFA, 298 K): \(\delta\) 1.96–2.42 (br, 204H, COCH\(_2\)CH\(_2\) from PBLG, COCH\(_2\) and NCH\(_2\)CH\(_2\)N from G1), 2.42–2.66 (br, 192H, COCH\(_2\)CH\(_2\) from PBLG), 4.58 (br, 96H, COCHNH), 5.12 (br, 192H, COOCH\(_3\)Ph), 7.15–7.25 (br, 480H, COOCH\(_2\)Ph), 8.10 (m, 100H, CONH). FT-IR (KBr): \(\nu\) (cm\(^{-1}\)) 3291 (N-H stretching), 3037 (C-H stretching of phenyl rings), 1735 (C=O stretching), 1653 (C=O stretching of \(\alpha\)-helix), 1545 (N-H bending of \(\alpha\)-helix).

**PBLG2 (B\(_{192}\)):** \(^1\)H NMR (300 MHz, CDCl\(_3\)+15 vol% TFA, 298 K): \(\delta\) 1.96–2.27 (br, 384H, COCH\(_2\)CH\(_2\) from PBLG), 2.27–2.66 (br, 420H, COCH\(_2\)CH\(_2\) from PBLG, COCH\(_2\), NCH\(_2\)CH\(_2\)N and NCH\(_2\)CH\(_2\)NH from G2), 4.58 (br, 192H, COCHNH), 5.12
FT-IR (KBr): $\nu$ (cm$^{-1}$) 3291 (N-H stretching), 3037 (C-H stretching of phenyl rings), 1735 (C=O stretching), 1653 (C=O stretching of $\alpha$-helix), 1545 (N-H bending of $\alpha$-helix).

**PBLG3** ($\mathcal{B}_{384}$): $^1$H NMR (300 MHz, CDCl$_3$+15 vol% TFA, 298 K): $\delta$ 1.96–2.27 (br, 768H, COCH$_2$CH$_2$ from PBLG), 2.27–2.66 (br, 852H, COCH$_2$CH$_2$ from PBLG, COCH$_3$, NCH$_2$CH$_2$N and NCH$_2$CH$_2$NH from G3), 4.58 (br, 384H, COCHNH), 5.12 (br, 768H, COOCH$_2$Ph), 7.15–7.25 (br, 1920H, COOCH$_2$Ph), 8.10 (m, 428H, CONH). FT-IR (KBr): $\nu$ (cm$^{-1}$) 3291 (N-H stretching), 3037 (C-H stretching of phenyl rings), 1735 (C=O stretching), 1653 (C=O stretching of $\alpha$-helix), 1545 (N-H bending of $\alpha$-helix).

**PBLG4** ($\mathcal{B}_{768}$): $^1$H NMR (300 MHz, CDCl$_3$+15 vol% TFA, 298 K): $\delta$ 1.96–2.27 (br, 768H, COCH$_2$CH$_2$ from PBLG), 2.27–2.66 (br, 948H, COCH$_2$CH$_2$ from PBLG, COCH$_3$, NCH$_2$CH$_2$N and NCH$_2$CH$_2$NH from G2), 4.58 (br, 768H, COCHNH), 5.12 (br, 1536H, COOCH$_2$Ph), 7.15–7.25 (br, 3840H, COOCH$_2$Ph), 8.10 (m, 860H, CONH). FT-IR (KBr): $\nu$ (cm$^{-1}$) 3291 (N-H stretching), 3037 (C-H stretching of phenyl rings), 1735 (C=O stretching), 1653 (C=O stretching of $\alpha$-helix), 1545 (N-H bending of $\alpha$-helix).

The $^1$H NMR spectra of PBLG agreed with the literature data. The number of repeating units, DP, of PBLG synthesized was calculated from $^1$H NMR using $DP = \frac{18I_c}{I_e+I_f-2I_c}$, $I_c$, $I_e$ and $I_f$ are the integration of peak at 5.12 ppm and 2.41-2.69 ppm and 1.96-2.41 ppm, respectively. The molecular weight of 8-armed PBLG
synthesized was calculated using $M_n = 516 + DP \times 219$. The values of the number of repeating unit DP and $M_n$ were tabulated in Table S1.

**Table S1** Molecular weight, molecular weight distribution, and repeating units of 8-armed star PBLG.

<table>
<thead>
<tr>
<th>entry</th>
<th>$aM_n$ (kg/mol)</th>
<th>$bM_n$ (kg/mol)</th>
<th>$cM_n$ (kg/mol)</th>
<th>$d$PDI</th>
<th>$e$DP</th>
<th>$8B_n$</th>
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<tr>
<td>PBLG1</td>
<td>25.1</td>
<td>22.5</td>
<td>23.4</td>
<td>1.17</td>
<td>96</td>
<td>$8B_{12}$</td>
</tr>
<tr>
<td>PBLG2</td>
<td>47.2</td>
<td>43.5</td>
<td>44.2</td>
<td>1.20</td>
<td>192</td>
<td>$8B_{24}$</td>
</tr>
<tr>
<td>PBLG3</td>
<td>91.5</td>
<td>85.5</td>
<td>86.9</td>
<td>1.18</td>
<td>384</td>
<td>$8B_{48}$</td>
</tr>
<tr>
<td>PBLG4</td>
<td>180.0</td>
<td>169.6</td>
<td>172.5</td>
<td>1.18</td>
<td>768</td>
<td>$8B_{96}$</td>
</tr>
</tbody>
</table>

$^a$Calculated. $^b$Determined by $^1$H NMR. $^c$Determined by GPC calibrated with PEO standard. $^d$PDI denoted molecular weight distribution of PBLG synthesized. $^e$DP denoted the number of repeating units of PBLG synthesized. DP was calculated from $^1$H NMR using $DP = 18I_c/(I_c+I_f - 2I_e)$, $I_c$, $I_e$ and $I_f$ are the integration of peak at 5.12 ppm and 2.41-2.69 ppm and 1.96-2.41 ppm, respectively.
**Synthesis of 1-(4-aminophenyl)-1,2,2-triphenylethene (I).**

A three-necked flask equipped with a magnetic stirrer was charged with zinc powder (7.85 g, 120 mmol) and 150 mL THF under N\textsubscript{2} atmosphere. The mixture was cooled to 0 °C, and TiCl\textsubscript{4} (6.5 mL, 60 mmol) was slowly added with the temperature below 10 °C. The suspending mixture was warmed to room temperature and stirred for 0.5 h, then heat to reflux for 2.5 h. The mixture was again cooled to 0 °C, charged with pyridine (2.5 mL, 30 mmol) and stirred for 10 min. 2.62 g of benzophenone (14.4 mmol) and 2.36 g of 4-aminobenzophenone (12 mmol) were added slowly. After addition, the reaction mixture was heated at reflux until the carbonyl compounds were consumed (monitored by TLC). The reaction was quenched with 10\% K\textsubscript{2}CO\textsubscript{3} aqueous solution, and filtered to remove solid. The product was taken up with CH\textsubscript{2}Cl\textsubscript{2}. The organic layer was collected and concentrated. The crude material was purified by flash chromatography to give the desired products. Yield 82%. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}), \textit{δ} (TMS, ppm): 3.40–3.64 (br, 2H, NH\textsubscript{2}), 6.36–6.40 (d, 2H, Ar–H), 6.76–6.82 (d, 2H, Ar–H), 6.94–7.11 (m, 15H, Ar–H).

**Synthesis of tetraphenylethene decorated PBLG (PBLG-TPE).**

Prescribed amount of PBLG, compound I and catalytical amount of 2-hydropyridine were dissolved in 50 mL of anhydrous THF. The mixture was stirred at 40 °C for 72 h in dark under N\textsubscript{2}. The product was precipitated by adding the reaction mixture dropwise to 500 mL of cold hexane with stirring, filtrated, and washed with hexane (100 mL× 3). The solid was dried in vacuum at 40 °C overnight to yield tetraphenylethene decorated PBLG (PBLG-TPE).
$B_{96}$-TPE2: $^1$H NMR (300 MHz, CDCl$_3$+15 vol% TFA, 298 K): $\delta$ 1.96–2.42 (br, 204H, COCH$_2$CH$_2$ from PBLG, COCH$_2$ and NCH$_2$CH$_2$N from G1), 2.42–2.66 (br, 192H, COCH$_2$CH$_2$ from PBLG), 4.58 (br, 96H, COCHNH), 5.12 (br, 188H, COOCH$_2$Ph), 6.90–7.10 (br, 36H, Ar–H), 7.15–7.25 (br, 480H, COOCH$_2$Ph), 8.10 (m, 100H, CONH). FT-IR (KBr): $\nu$ (cm$^{-1}$) 3291 (N–H stretching), 3037 (C–H stretching of phenyl rings), 1735 (C=O stretching), 1653 (C=O stretching of $\alpha$-helix), 1545 (N–H bending of $\alpha$-helix). FT-IR spectra of PBLG-TPE were shown in Fig. 1.

$B_{192}$-TPE2: $^1$H NMR (300 MHz, CDCl$_3$+15 vol% TFA, 298 K): $\delta$ 1.96–2.27 (br, 384H, COCH$_2$CH$_2$ from PBLG), 2.27–2.66 (br, 420H, COCH$_2$CH$_2$ from PBLG, COCH$_2$, NCH$_2$CH$_2$N and NCH$_2$CH$_2$NH from G2), 4.58 (br, 192H, COCHNH), 5.12 (br, 376H, COOCH$_2$Ph), 6.90–7.10 (br, 72H, Ar–H), 7.15–7.25 (br, 960H, COOCH$_2$Ph), 8.10 (m, 212H, CONH). FT-IR (KBr): $\nu$ (cm$^{-1}$) 3291 (N–H stretching), 3037 (C–H stretching of phenyl rings), 1735 (C=O stretching), 1653 (C=O stretching of $\alpha$-helix), 1545 (N–H bending of $\alpha$-helix).

$B_{384}$-TPE2: $^1$H NMR (300 MHz, CDCl$_3$+15 vol% TFA, 298 K): $\delta$ 1.96–2.27 (br, 768H, COCH$_2$CH$_2$ from PBLG), 2.27–2.66 (br, 852H, COCH$_2$CH$_2$ from PBLG, COCH$_2$, NCH$_2$CH$_2$N and NCH$_2$CH$_2$NH from G3), 4.58 (br, 384H, COCHNH), 5.12 (br, 753H, COOCH$_2$Ph), 6.90–7.10 (br, 146H, Ar–H), 7.15–7.25 (br, 1920H, COOCH$_2$Ph), 8.10 (m, 428H, CONH). FT-IR (KBr): $\nu$ (cm$^{-1}$) 3291 (N–H stretching), 3037 (C–H stretching of phenyl rings), 1735 (C=O stretching), 1653 (C=O stretching of $\alpha$-helix), 1545 (N–H bending of $\alpha$-helix).

$B_{768}$-TPE2: $^1$H NMR (300 MHz, CDCl$_3$+15 vol% TFA, 298 K): $\delta$ 1.96–2.27 (br,
768H, COCH$_2$CH$_2$ from PBLG), 2.27–2.66 (br, 948H, COCH$_2$CH$_2$ from PBLG, COCH$_2$, NCH$_2$CH$_2$N and NCH$_2$CH$_2$NH from G2), 4.58 (br, 768H, COCHNH), 5.12 (br, 1506H, COOCH$_2$Ph), 6.90–7.10 (br, 292H, Ar–H), 7.15–7.25 (br, 3840H, COOCH$_2$Ph), 8.10 (m, 860H, CONH). FT-IR (KBr): $\nu$ (cm$^{-1}$) 3291 (N–H stretching), 3037 (C–H stretching of phenyl rings), 1735 (C=O stretching), 1653 (C=O stretching of $\alpha$-helix), 1545 (N–H bending of $\alpha$-helix).

$B_{192}$-TPE1: $^1$H NMR (300 MHz, CDCl$_3$+15 vol% TFA, 298 K): $\delta$ 1.96–2.27 (br, 384H, COCH$_2$CH$_2$ from PBLG), 2.27–2.66 (br, 420H, COCH$_2$CH$_2$ from PBLG, COCH$_2$, NCH$_2$CH$_2$N and NCH$_2$CH$_2$NH from G2), 4.58 (br, 192H, COCHNH), 5.12 (br, 380H, COOCH$_2$Ph), 6.90–7.10 (br, 36H, Ar–H), 7.15–7.25 (br, 960H, COOCH$_2$Ph), 8.10 (m, 212H, CONH). FT-IR (KBr): $\nu$ (cm$^{-1}$) 3291 (N–H stretching), 3037 (C–H stretching of phenyl rings), 1735 (C=O stretching), 1653 (C=O stretching of $\alpha$-helix), 1545 (N–H bending of $\alpha$-helix).

$B_{192}$-TPE4: $^1$H NMR (300 MHz, CDCl$_3$+15 vol% TFA, 298 K): $\delta$ 1.96–2.27 (br, 384H, COCH$_2$CH$_2$ from PBLG), 2.27–2.66 (br, 420H, COCH$_2$CH$_2$ from PBLG, COCH$_2$, NCH$_2$CH$_2$N and NCH$_2$CH$_2$NH from G2), 4.58 (br, 192H, COCHNH), 5.12 (br, 369H, COOCH$_2$Ph), 6.90–7.10 (br, 146H, Ar–H), 7.15–7.25 (br, 960H, COOCH$_2$Ph), 8.10 (m, 212H, CONH). FT-IR (KBr): $\nu$ (cm$^{-1}$) 3291 (N–H stretching), 3037 (C–H stretching of phenyl rings), 1735 (C=O stretching), 1653 (C=O stretching of $\alpha$-helix), 1545 (N–H bending of $\alpha$-helix).

$B_{192}$-TPE5: $^1$H NMR (300 MHz, CDCl$_3$+15 vol% TFA, 298 K): $\delta$ 1.96–2.27 (br, 384H, COCH$_2$CH$_2$ from PBLG), 2.27–2.66 (br, 420H, COCH$_2$CH$_2$ from PBLG,
COCH₂, NCH₂CH₂N and NCH₂CH₂NH from G2), 4.58 (br, 192H, COCHNH), 5.12 (br, 365H, COOCH₂Ph), 6.90–7.10 (br, 182H, Ar–H), 7.15–7.25 (br, 960H, COOCH₂Ph), 8.10 (m, 212H, CONH). FT-IR (KBr): ν (cm⁻¹) 3291 (N–H stretching), 3037 (C–H stretching of phenyl rings), 1735 (C=O stretching), 1653 (C=O stretching of α-helix), 1545 (N–H bending of α-helix).

Molar percentage of TPE in PBLG-TPE was determined by 1H NMR using \( m_{\text{TPE}} = 1 - \frac{I_d}{2I_e} \), where \( I_d \) and \( I_e \) were the integration of peak at 5.12 and 4.58 ppm, respectively.
**Fig. S2** $^1$H NMR spectra of 8-armed star PBLG-TPE.

![NMR spectra](image)

**Fig. S3** (a) UV-vis spectra of compound 2/THF solution at various concentrations and (b) the plots of absorbance (335 nm) against concentration of compound 2.
Calculation of radiative and non-radiative decay rate constants.

Fluorescence typically follows first-order kinetics:

$$[S] = [S]_0 e^{-t/\tau}$$  \hspace{1cm} (S1)

$[S]$ is the concentration of exited state molecules at time $t$, $[S]_0$ is the initial concentration and $\tau$ is the fluorescence lifetime.

Decay rate ($k$) is the inverse of lifetime, consisting of radiative and non-radiative decay rate constants:

$$k = k_{rad} + k_{nrad}$$  \hspace{1cm} (S2)

where $k_{rad}$ is the radiative decay rate constant and $k_{nrad}$ is the nonradiative decay rate constant. The quantum yield (QE) is defined as the fraction of emission process in which emission of light is involved:

$$QE = \frac{k_{rad}}{k_{rad} + k_{nrad}}$$  \hspace{1cm} (S3)

The values of radiative and non-radiative rate constants of TPE and TPE-CDs were
tabulated in Table 1.

**Fig. S5** DSC curve for $B_{192}$-TPE2.

**Fig. S6** XRD spectra for $B_{192}$-TPE2 at various temperatures.
1  (a) X. Y. Zhu, L. J. Zhu, Y. F. Shi, C. L. Tu, R. B. Wang, Y. Pang, F. Qiu, D.

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W. H. Daly and D. Poche, *Tetrahedron Lett.*, 1988, **29**, 5859–5862; (c) A.
Kros, H. R. Marsden, J. W. Handgraaf, F. Nudelman and N. A. J. M.

3  G. L. Zhang, F. Liang, X. M. Song, D. L. Liu, M. J. Li and Q. H. Wu,