Synthesis of decacationic [60]fullerene decaiodides giving photoinduced production of superoxide radicals and effective PDT-mediation on antimicrobial photoinactvation

Min Wang [a], Satyanarayana Maragani [a], Liyi Huang [b,c], Seaho Jeon [a], Taizoon Canteenwala [a], Michael R. Hamblin [b,c,d,*], Long Y. Chiang [a,e,*]

[a] *Department of Chemistry, Institute of Nanoscience and Engineering Technology, University of Massachusetts, Lowell, MA 01854, United States*

[b] *Wellman Center for Photomedicine, Massachusetts General Hospital, Boston, MA 02114, United States*

[c] *Department of Dermatology, Harvard Medical School, Boston, MA 02115, United States*

[d] *Harvard–MIT Division of Health Sciences and Technology, Cambridge, MA 02139, United States*

[e] *Department of Laboratory Medicine and Pathobiology, University of Toronto, Toronto, ON M5S 1A8, Canada*

Supporting Information

Figure S1. ^{1}H NMR spectra of (a) **2** in $CDCl_3$, (b) **3** in $CDCl_3$, (c) **4** in $CDCl_3$, (d) **5** in DMSO-d_6, and (e) **1**-$(I^-)_{10}$ in DMSO-d_6 in Scheme 1.

Figure S2. FT-IR spectra of (a) $M(C_3N_6^+C_3)_2$ (**5**), (b) $C_{60}[>M(C_3N_6^+C_3)_2]$-$(I^-)_{10}$ [**1**-$(I^-)_{10}$], and (c) $C_{60}[>M(C_3N_6^+C_3)_2]$-($TFA^-)_{10}$ [**1**-$(TFA^-)_{10}$] in Scheme 1.

Figure S3. FT-IR spectra of (a) $C_{60}[>M(t\text{-}Bu)_2]$ (**6**), (b) precursor arm $M(C_3N_6^+C_3H)_2$, (c) $C_{60}[>M(C_3N_6^+C_3H)_2]$ **7**, (d) $C_{60}[>M(C_3N_6^+C_3)_2]$-$(I^-)_{10}$ [**1**-$(I^-)_{10}$], and (e) $C_{60}[>M(C_3N_6^+C_3)_2]$-($TFA^-)_{10}$ [**1**-$(TFA^-)_{10}$] in Scheme 2.

Figure S4. ^{13}C NMR spectra of (a) **6** in $CDCl_3$–CS_2, (b) **7** in DMF-d_7–$CDCl_3$–CS_2, and (c) $C_{60}[>M(C_3N_6^+C_3)_2]$-($TFA^-)_{10}$ [**1**-$(TFA^-)_{10}$] in DMSO-d_6–$CDCl_3$–CS_2 in Scheme 2.

Figure S5. Analysis of fragmented mass ions based on both MALDI-TOF and ESI mass spectra of $C_{60}[>M(C_3N_6^+C_3)_2]$-$(I^-)_{10}$ [**1**-$(I^-)_{10}$] in Fig. 3.

Figure S6. Illumination time-dependent fluorescent intensity increase of fluorescein probe TFFC in PBS media (*pH* 7.4) in the presence of (a) xanthine/xanthine oxidase by the addition in two steps, (b) xanthine/xanthine oxidase followed by the addition of superoxide dismutase, and (c) xanthine/xanthine oxidase and superoxide dismutase at the same time, showing clearly the fluorescent intensity increase of the fluorescein probe rising from the reaction of DNBs-TFFC with superoxide radical ($O_2^{-}\cdot$). The fluorometric traces were collected at λ_{em} 530 nm with λ_{ex} 480 nm.

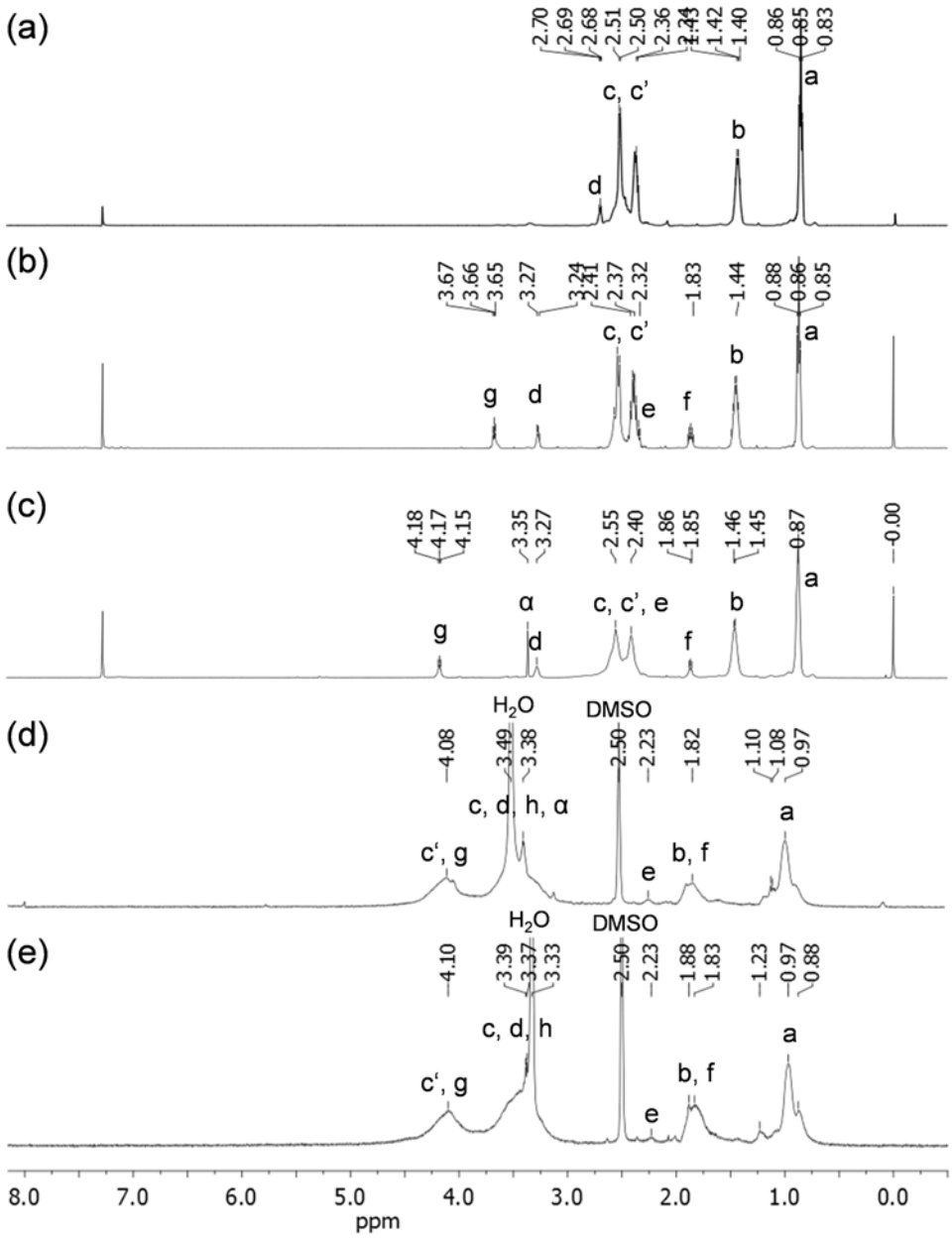

Fig. S1. ^{1}H NMR spectra of (a) **2** in $CDCl_3$, (b) **3** in $CDCl_3$, (c) **4** in $CDCl_3$, (d) **5** in DMSO-d_6, and (e) **1**-$(\Gamma)_{10}$ in DMSO-d_6 in Scheme 1.

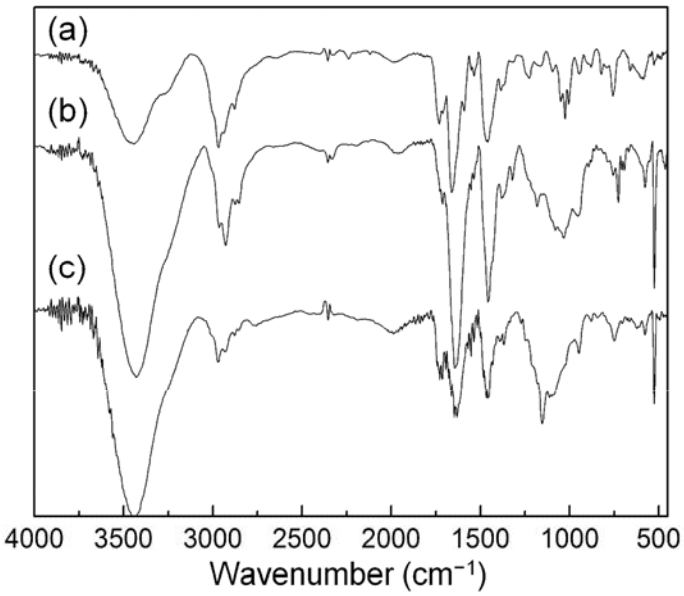

Fig. S2. FT-IR spectra of (a) $M(C_3N_6^+C_3)_2$ (**5**), (b) $C_{60}[>M(C_3N_6^+C_3)_2]$-$(I^-)_{10}$ [**1**-$(I^-)_{10}$], and (c) $C_{60}[>M(C_3N_6^+C_3)_2]$-$(TFA^-)_{10}$ [**1**-$(TFA^-)_{10}$] in Scheme 1.

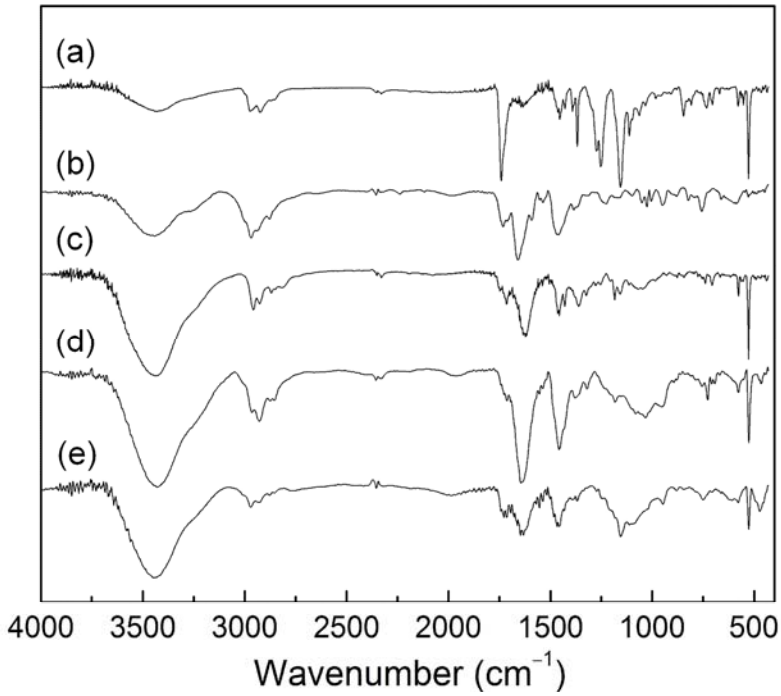

Fig. S3. FT-IR spectra of (a) $C_{60}[>M(t\text{-Bu})_2]$ (**6**), (b) precursor arm $M(C_3N_6^+C_3H)_2$, (c) $C_{60}[>M(C_3N_6^+C_3H)_2]$ **7**, (d) $C_{60}[>M(C_3N_6^+C_3)_2]$-$(I^-)_{10}$ [**1**-$(I^-)_{10}$], and (e) $C_{60}[>M(C_3N_6^+C_3)_2]$-$(TFA^-)_{10}$ [**1**-$(TFA^-)_{10}$] in Scheme 2.

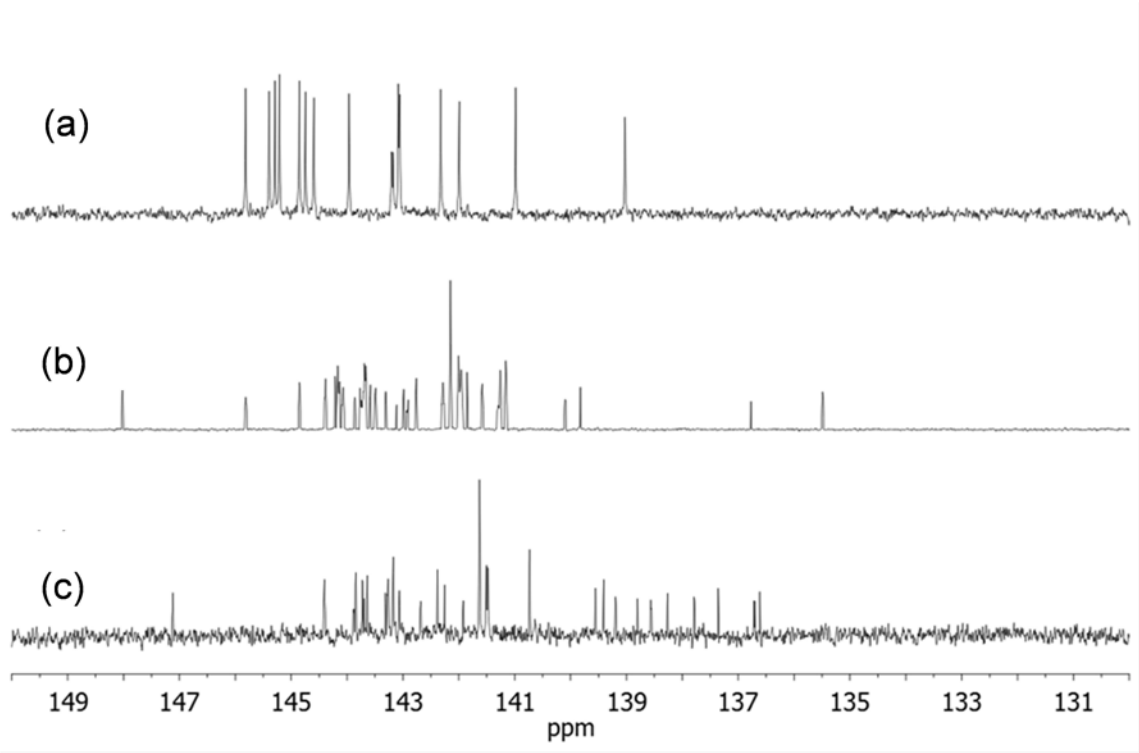

Fig. S4. ^{13}C NMR spectra of (a) **6** in $CDCl_3$−CS_2,, (b) **7** in DMF-d_7−$CDCl_3$−CS_2, and (c) $C_{60}[>M(C_3N_6{}^+C_3)_2]$-($TFA^-)_{10}$ [**1**-$(TFA^-)_{10}$] in DMSO-d_6−$CDCl_3$−CS_2 in Scheme 2.

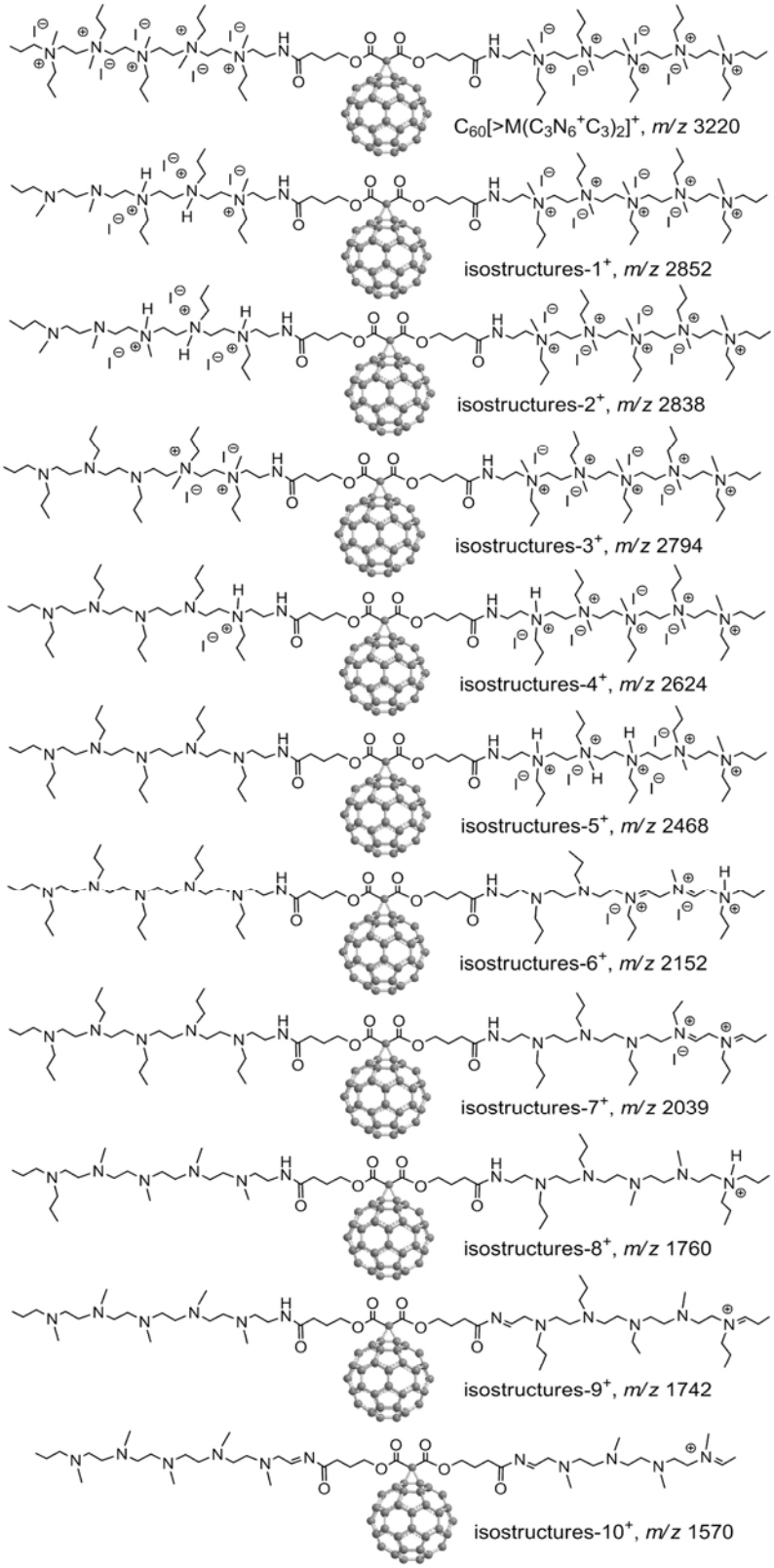

Fig. S5. Analysis of fragmented mass ions based on both MALDI-TOF and ESI mass spectra of $C_{60}[>M(C_3N_6^+C_3)_2]$-$(I^-)_{10}$ [**1**-$(I^-)_{10}$] in Fig. 3.

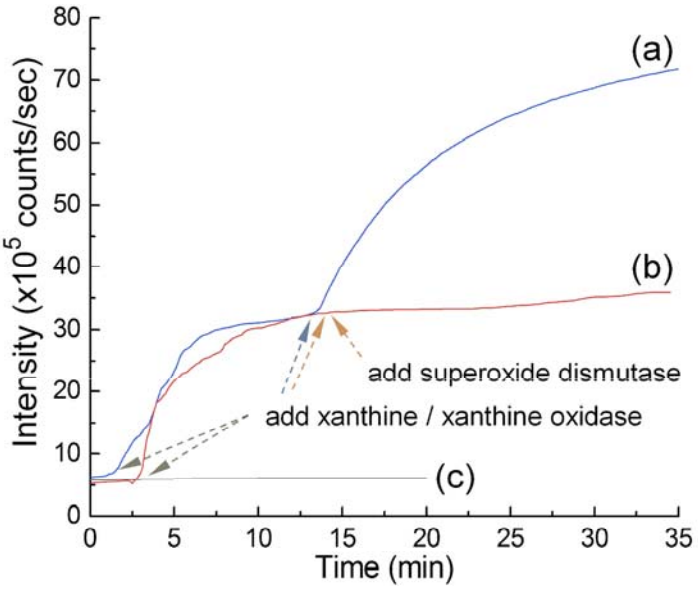

Fig. S6. Illumination time-dependent fluorescent intensity increase of fluorescein probe TFFC in PBS media (*pH* 7.4) in the presence of (a) xanthine/xanthine oxidase by the addition in two steps, (b) xanthine/xanthine oxidase followed by the addition of superoxide dismutase, and (c) xanthine/xanthine oxidase and superoxide dismutase at the same time, showing clearly the fluorescent intensity increase of the fluorescein probe rising from the reaction of DNBs-TFFC with superoxide radical ($O_2^{-}\cdot$). The fluorometric traces were collected at λ_{em} 530 nm with λ_{ex} 480 nm.