Electronic supplementary information

Poly-Histidine Grafting Leading to Fishbone-Like Architectures

Vincenzo Razzano,^a Marco Paolino,^a Annalisa Reale,^a Germano Giuliani,^a Roberto Artusi,^b

Gianfranco Caselli,^b Michela Visintin,^b Francesco Makovec,^b Alessandro Donati,^a Gianluca

Giorgi,^a Francesca Villafiorita-Monteleone,^c Chiara Botta,^c Andrea Cappelli.^{*,a}

^aDipartimento di Biotecnologie, Chimica e Farmacia and European Research Centre for Drug

Discovery and Development, Università di Siena, Via A. Moro 2, 53100 Siena, Italy,

^bRottapharm Biotech S.p.A., Via Valosa di Sopra 9, 20900 Monza, Italy,

^cIstituto per lo Studio delle Macromolecole (CNR), Via E. Bassini 15, 20133 Milano, Italy.

E-mail: andrea.cappelli@unisi.it.

Table of contents:

ESI mass spectrum of Ac-His-6-MBHA-1d material NMR spectra of compounds 1a-e, 2a-d, 3a-c, 5, 6a,b, 8 Photoluninescence of the polymeric materials obtained by exciting at different wavelengths

page S2 pages S3-S18

page S19



Figure ESI-1. ESI mass spectrum (negative-ion mode) of Ac-His-6-MBHA-1d material.



Figure ESI-2. ¹H NMR (500 MHz, CDCl₃) of methyl 2-[acetoxy[6-(prop-2-ynyloxy)naphthalen-2-yl]methyl]acrylate (**1a**).



Figure ESI-3. ¹³C NMR (125 MHz, CDCl₃) of methyl 2-[acetoxy[6-(prop-2-ynyloxy)naphthalen-2-yl]methyl]acrylate (1a).



Figure ESI-4. ¹H NMR (500 MHz, $CDCl_3$) of methyl 2-[acetoxy(6-ethynylnaphthalen-2-yl)methyl]acrylate (1b).



Figure ESI-5. ¹³C NMR (125 MHz, CDCl₃) of methyl 2-[acetoxy(6-ethynylnaphthalen-2-yl)methyl]acrylate (**1b**).



Figure ESI-6. ¹H NMR (400 MHz, CDCl₃) of 2-(methoxycarbonyl)-1-[6-(prop-2-ynyloxy)naphthalen-2-yl]allyl 2,5,8,11,14,17,20,23,26,29,32,35-dodecaoxaoctatriacontan-38-oate (1c).



Figure ESI-7. ¹³C NMR (125 MHz, CDCl₃) of 2-(methoxycarbonyl)-1-[6-(prop-2-ynyloxy)naphthalen-2-yl]allyl 2,5,8,11,14,17,20,23,26,29,32,35-dodecaoxaoctatriacontan-38-oate (1c).



Figure ESI-8. ¹H NMR (500 MHz, CDCl₃) of 1-(6-ethynylnaphthalen-2-yl)-2- (methoxycarbonyl)allyl 2,5,8,11,14,17,20,23,26,29,32,35-dodecaoxaoctatriacontan-38-oate (1d).



Figure ESI-9. ¹³C NMR (125 MHz, CDCl₃) of 1-(6-ethynylnaphthalen-2-yl)-2-(methoxycarbonyl)allyl 2,5,8,11,14,17,20,23,26,29,32,35-dodecaoxaoctatriacontan-38-oate (1d).



Figure ESI-10. ¹H NMR (500 MHz, CDCl₃) of methyl 2-[[6-[1-(2,5,8,11,14,17,20,23,26-nonaoxaoctacosan-28-yl]-1H-1,2,3-triazol-4-yl]naphthalen-2-yl](acetoxy)methyl]acrylate (1e).



Figure ESI-11. ¹³C NMR (125 MHz, CDCl₃) of methyl 2-[[6-[1-(2,5,8,11,14,17,20,23,26-nonaoxaoctacosan-28-yl]-1H-1,2,3-triazol-4-yl]naphthalen-2-yl](acetoxy)methyl]acrylate (1e).



Figure ESI-12. ¹H NMR (500 MHz, CDCl₃) of (*E*)-methyl 2-[(1*H*-imidazol-1-yl)methyl]-3-[6-(prop-2-ynyloxy)naphthalen-2-yl]acrylate (**2a**).



Figure ESI-13. ¹³C NMR (125 MHz, CDCl₃) of (*E*)-methyl 2-[(1*H*-imidazol-1-yl)methyl]-3-[6-(prop-2-ynyloxy)naphthalen-2-yl]acrylate (**2a**).



Figure ESI-14. ¹H NMR (500 MHz, CDCl₃) of (*E*)-methyl 2-[(1*H*-imidazol-1-yl)methyl]-3-(6-ethynylnaphthalen-2-yl)acrylate (**2b**).



Figure ESI-15. ¹³C NMR (125 MHz, CDCl₃) of (*E*)-methyl 2-[(1*H*-imidazol-1-yl)methyl]-3-(6-ethynylnaphthalen-2-yl)acrylate (**2b**).



Figure ESI-16. ¹H NMR (500 MHz, CDCl₃) of (*E*)-2-acetamido-3-[1-[3-(6-ethynylnaphthalen-2-yl)-2-(methoxycarbonyl)allyl]-1*H*-imidazol-4-yl]propanoic acid (**2c**).



Figure ESI-17. ¹³C NMR (125 MHz, CDCl₃) of (*E*)-2-acetamido-3-[1-[3-(6-ethynylnaphthalen-2-yl)-2-(methoxycarbonyl)allyl]-1*H*-imidazol-4-yl]propanoic acid (**2c**).



Figure ESI-18. ¹H NMR (500 MHz, CDCl₃) of (*E*)-methyl 2-[(1*H*-imidazol-1-yl)methyl]-3-[6-[1-[2-[2-(2-methoxyethoxy]ethyl]-1*H*-1,2,3-triazol-4-yl]naphthalen-2-yl]acrylate (**2d**).



Figure ESI-19. ¹³C NMR (125 MHz, CDCl₃) of (*E*)-methyl 2-[(1*H*-imidazol-1-yl)methyl]-3-[6-[1-[2-[2-(2-methoxyethoxy]ethyl]-1*H*-1,2,3-triazol-4-yl]naphthalen-2-yl]acrylate (**2d**).



Figure ESI-20. ¹H NMR (400 MHz, CDCl₃) of 1,3-bis[[(E)-2-(methoxycarbonyl)-3-[6-(prop-2-ynyloxy)naphthalen-2-yl]allyl]-1H-imidazol-3-ium chloride (**3a**).



Figure ESI-21. ¹³C NMR (125 MHz, CDCl₃) of 1,3-bis[[(E)-2-(methoxycarbonyl)-3-[6-(prop-2-ynyloxy)naphthalen-2-yl]allyl]-1H-imidazol-3-ium chloride (**3a**).



Figure ESI-22. ¹H NMR (400 MHz, CDCl₃) of 1,3-bis[[(E)-3-(6-ethynylnaphthalen-2-yl)-2-(methoxycarbonyl)allyl]-1H-imidazol-3-ium chloride (**3b**).



Figure ESI-23. ¹³C NMR (125 MHz, CDCl₃) of 1,3-bis[[(E)-3-(6-ethynylnaphthalen-2-yl)-2-(methoxycarbonyl)allyl]-1*H*-imidazol-3-ium chloride (**3b**).



Figure ESI-24. ¹H NMR (500 MHz, CDCl₃) of 2-acetamido-3-[1,3-bis[(*E*)-3-(6-ethynylnaphthalen-2-yl)-2-(methoxycarbonyl)allyl]-1*H*-imidazol-3-ium-4-yl]propanoate (**3c**).



Figure ESI-25. ¹³C NMR (125 MHz, CDCl₃) of 2-acetamido-3-[1,3-bis[(E)-3-(6-ethynylnaphthalen-2-yl)-2-(methoxycarbonyl)allyl]-1H-imidazol-3-ium-4-yl]propanoate (**3c**).



Figure ESI-26. ¹H NMR (500 MHz, CDCl₃) of 6-(prop-2-ynyloxy)-2-naphthaldehyde (5).



Figure ESI-27. ¹³C NMR (125 MHz, CDCl₃) of 6-(prop-2-ynyloxy)-2-naphthaldehyde (5).



Figure ESI-28. ¹H NMR (400 MHz, CDCl₃) of methyl 2-[hydroxyl[6-(prop-2-ynyloxy)naphthalen-2-yl]methyl]acrylate (**6a**).



Figure ESI-29. ¹³C NMR (125 MHz, CDCl₃) of methyl 2-[hydroxyl[6-(prop-2-ynyloxy)naphthalen-2-yl]methyl]acrylate (**6a**).



Figure ESI-30. ¹H NMR (500 MHz, CDCl₃) of methyl 2-[(6-ethynylnaphthalen-2-yl)(hydroxy)methyl]acrylate (**6b**).



Figure ESI-31. ¹³C NMR (125 MHz, CDCl₃) of methyl 2-[(6-ethynylnaphthalen-2-yl)(hydroxy)methyl]acrylate (**6b**).



Figure ESI-32. ¹H NMR (500 MHz, CDCl₃) of 6-ethynyl-2-naphthaldehyde (8).



Figure ESI-33. ¹³C NMR (125 MHz, CDCl₃) of 6-ethynyl-2-naphthaldehyde (8).



Figure ESI-34. Photoluninescence of polymeric material Ac-His-6-MBHA-1d obtained by exciting at different wavelengths.



Figure ESI-35. Photoluninescence of polymeric material **Ac-His-6-MBHA-1e** obtained by exciting at different wavelengths.