Pergamon

Tetrahedron Letters 43 (2002) 7507–7511

TETRAHEDRON
LETTERS

Synthesis of dumbbell-shaped bis-(pyrazolino[60]fullerene)-oligophenylenevinylene derivatives

María J. Gómez-Escalonilla,[a] Fernando Langa,[a,*] Jean-Michel Rueff,[b] Laurence Oswald[b] and Jean-François Nierengarten[b,*]

[a]*Facultad de Ciencias del Medio Ambiente, Universidad de Castilla-La Mancha, 45071 Toledo, Spain*
[b]*Groupe des Matériaux Organiques, Institut de Physique et Chimie des Matériaux de Strasbourg, Université Louis Pasteur et CNRS, 23 rue du Loess, 67037 Strasbourg Cedex, France*

Received 21 August 2002; accepted 23 August 2002

Abstract—Symmetrically substituted oligophenylenevinylene (OPV) derivatives bearing terminal *p*-nitrophenyl-hydrazone groups have been prepared and used for the synthesis of dumbbell-shaped bis-(pyrazolino[60]fullerene)-OPV systems. © 2002 Elsevier Science Ltd. All rights reserved.

The design of molecules bearing covalently linked electron donors to [60]fullerene (C_{60}) have received increasing attention in the past few years as these systems can be used in artificial photosynthesis and for photoelectronic applications.[1] As part of this research, compounds combining C_{60} with π-conjugated oligomers are of particular interest.[2–5] On one hand, they provide entry into photoinduced intramolecular processes such as energy and electron transfer.[3] On the other hand, such hybrid compounds can be used for the preparation of solar cells allowing a detailed structure–activity exploration for a better understanding of the photovoltaic system.[4] As far as the synthesis of such fullerene derivatives is concerned, the 1,3-dipolar cycloaddition of C_{60} with an azomethine ylide generated in situ from an oligomer containing an aldehyde functionality and *N*-methylglycine is the most widely used strategy.[2–5] The resulting fulleropyrrolidines are usually obtained in good yields but an asymmetric C atom is generated during the cycloaddition reaction. Therefore, the use of this methodology for the preparation of π-conjugated systems bearing more than one fullerene sphere yields diastereomeric mixtures.[5] In this communication, we show that oligophenylenevinylene (OPV) derivatives substituted with two fullerene moieties can be obtained by a 1,3-dipolar cycloaddition of C_{60} with bis-nitrilimines which were themselves generated in a one pot procedure[6] from the corresponding bis-hydrazones. Since no stereogenic centers are produced during the reaction, the dumbbell-shaped bis-(pyrazolino[60]fullerene) OPV derivatives are obtained in a pure form.

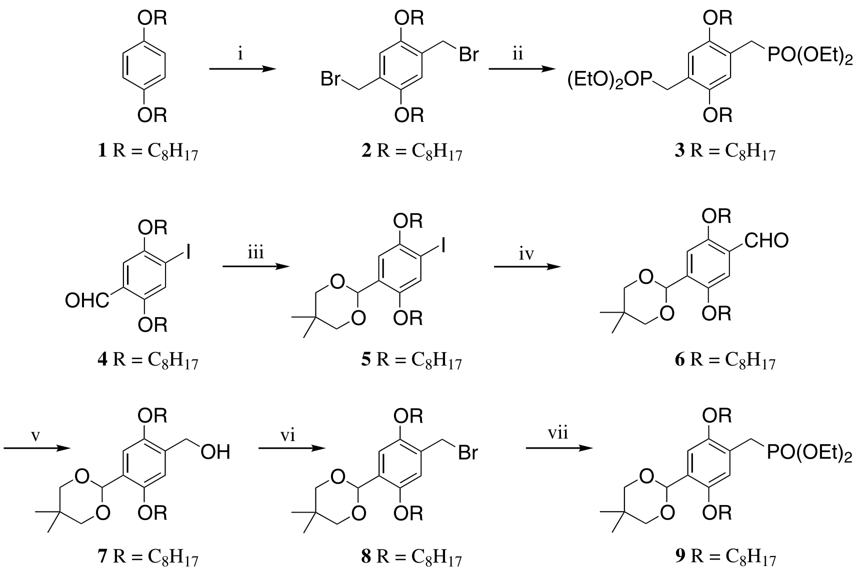
The strategy employed for the preparation of the functionalized OPV precursors is based upon Wittig–Horner type chemistry.[7] To this end, the key building blocks **3** and **9** were prepared first (Scheme 1). Bromomethylation of 1,4-bis(octyloxy)benzene **1**, by treatment with paraformaldehyde and HBr in acetic acid at 65°C, afforded **2** in 70% yield. Compound **2** was then converted to the bis-phosphonate **3** in 91% yield by a Michaelis–Arbuzov reaction. Compound **4** was prepared in two steps from **1** according to a previously reported method.[2e] Reaction of **4** with 2,2-dimethylpropane-1,3-diol in refluxing benzene in the presence of a catalytic amount of *p*-toluenesulfonic acid (TsOH) gave the protected aldehyde **5** in 87% yield. Subsequent treatment with *n*-BuLi in Et_2O at 0°C followed by quenching with dry DMF afforded aldehyde **6** in 86% yield. $LiAlH_4$ reduction then yielded alcohol **7** which, after treatment with CBr_4/PPh_3, gave bromide **8**. Phosphonate **9** was finally obtained in 99% yield by reaction of **8** with triethylphosphite under Michaelis–Arbuzov conditions.

Treatment of aldehyde **6** with bis-phosphonate **3** in THF in the presence of *t*-BuOK afforded the targeted OPV trimer, but as an *E*:*Z* isomer mixture (Scheme 2). The latter observation is quite surprising, as the reaction of benzylic phosphonates with aromatic aldehydes under Wittig–Horner conditions is generally stereose-

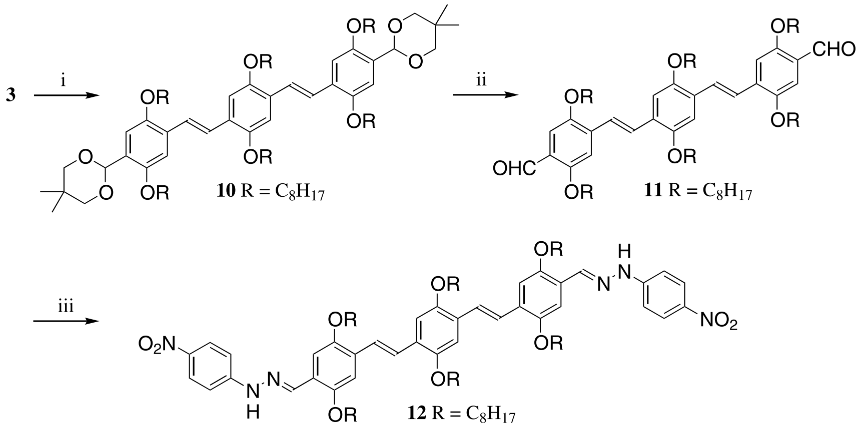
---

* Corresponding authors. E-mail: flanga@amb-to.uclm.es; niereng@ipcms.u-strasbg.fr

0040-4039/02/$ - see front matter © 2002 Elsevier Science Ltd. All rights reserved.
PII: S0040-4039(02)01769-0



Scheme 1. *Reagents and conditions*: (i) HBr, paraformaldehyde, AcOH, 65°C, 2 h (70%); (ii) $P(OEt)_3$, 150°C, 6 h (91%); (iii) 2,2-dimethylpropane-1,3-diol, TsOH (cat.), benzene, Δ, Dean Stark trap, 48 h (87%); (iv) *n*-BuLi, Et_2O, 0°C, 1 h, then DMF, 0°C to room temperature, 4 h (86%); (v) $LiAlH_4$, THF, 0°C, 4 h (80%); (vi) CBr_4, PPh_3, THF, 0°C to room temperature, 4 h (85%); (vii) $P(OEt)_3$, 150°C, 4 h (99%).

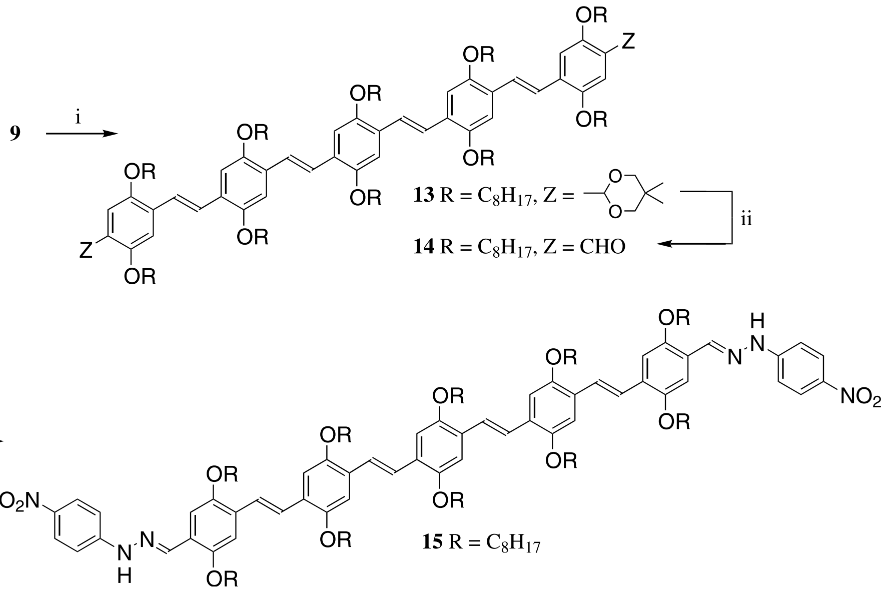


Scheme 2. *Reagents and conditions*: (i) **6**, *t*-BuOK, THF, 0°C, 1 h, then I_2 (cat.), toluene, Δ, 12 h (80%); (ii) CF_3CO_2H, CH_2Cl_2, H_2O, room temperature, 4 h (95%); (iii) *p*-nitrophenylhydrazine, AcOH, EtOH, Δ, 3.5 h (99%).

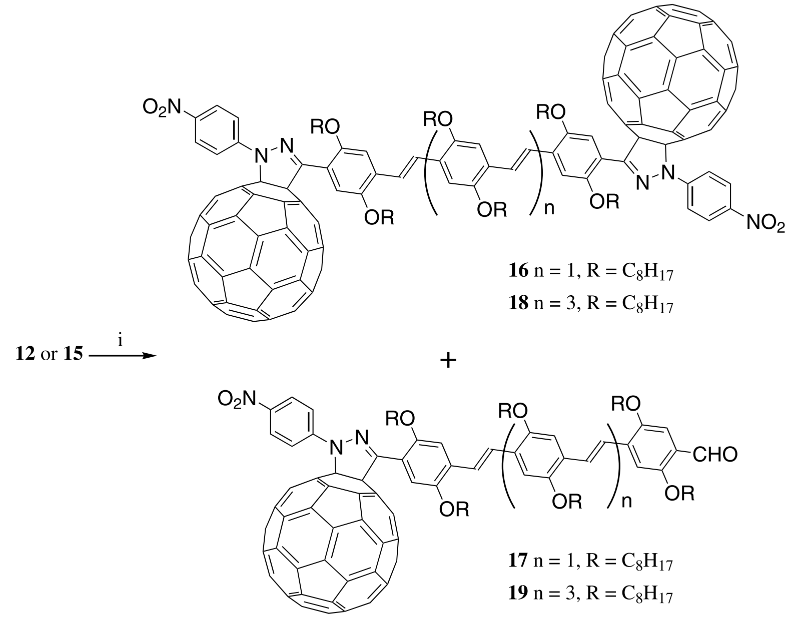
lective, leading to the *E* isomer only.[7] In the present case, steric hindrance resulting from the presence of the octyloxy group in the *ortho* position of the reactive groups in both **3** and **6** may explain the lack of *E*:*Z* selectivity. The isomerization of the isomeric mixture to the all-*E* derivative **10** was easily achieved by treatment with a catalytic amount of iodine in refluxing toluene and trimer **10** was thus obtained in 80% yield. Subsequent deprotection with CF_3CO_2H in CH_2Cl_2/H_2O afforded bis-aldehyde **11** in 95% yield. The *E* configuration of the double bonds in **11** was confirmed by a coupling constant of ca. 17 Hz for the AB system corresponding to the vinylic protons in the ^1H NMR spectrum. Bis-hydrazone **12** was then obtained in 99% yield from aldehyde **11** and *p*-nitrophenylhydrazine in refluxing ethanol in the presence of acetic acid.

The preparation of the corresponding OPV pentamer **15** is depicted in Scheme 3. Reaction of bis-aldehyde **11** with phosphonate **9** under Wittig–Horner conditions followed by treatment with a catalytic amount of iodine in refluxing toluene gave the all-*E* OPV pentamer **13** in 51% yield. Deprotection, by treatment with CF_3CO_2H in CH_2Cl_2/H_2O, followed by reaction of the resulting bis-aldehyde **14** with *p*-nitrophenylhydrazine in refluxing ethanol in the presence of acetic acid afforded the bis-hydrazone **15** in 83% yield.

Treatment of bis-hydrazone **12** with *N*-chlorosuccinimide (NCS) and pyridine in dry chloroform, followed by reaction of the resulting bis-nitrilimine intermediate with C_{60} in chlorobenzene in the presence of Et_3N at room temperature, afforded the desired dumbbell-shaped derivative **16** in 27% yield (Scheme 4). Interestingly, in addition to **16**, the monosubstituted derivative **17** was also isolated from the reaction mixture; the aldehyde group in **17** originates most probably from the hydrolysis of unreacted hydrazone moieties during the



Scheme 3. *Reagents and conditions*: (i) **11**, *t*-BuOK, THF, 0°C to room temperature, 2 h, then I_2 (cat.), toluene, Δ, 12 h (51%); (ii) CF_3CO_2H, CH_2Cl_2, H_2O, room temperature, 3 h (88%); (iii) *p*-nitrophenylhydrazine, AcOH, EtOH, Δ, 3.3 h (83%).



Scheme 4. *Reagents and conditions*: (i) NCS, pyridine, $CHCl_3$, 0°C to room temperature, then C_{60}, Et_3N, chlorobenzene, room temperature, 1 h [from **12**: **16** (27%) and **17** (57.5%); from **15**: **18** (10%) and **19** (19%)].

work-up procedure. Following the same procedure, the reaction of bis-hydrazone **15** with NCS and subsequent reaction with C_{60} at room temperature gave the bis-(pyrazolino[60]fullerene) OPV derivative **18** and the monosubstituted compound **19** in 10 and 19% yields, respectively. Due to the good solubility brought about by the octyloxy groups, the C_{60}-OPV derivatives **16**–**19** were easily characterized by ^1H and ^{13}C NMR.[8] The structures of **16**–**19** were also confirmed by their MALDI-TOF mass spectra showing the expected molecular ion peaks.[8]

The absorption spectra of **16**–**19** correspond to the sum of the spectra of their component subunits, indicating that there are no significant ground state interactions between the different chromophores. As depicted in Fig. 1, the UV–vis spectra of **16** recorded in CH_2Cl_2 shows the characteristic absorption features of a pyrazolino[60]fullerene derivative as well as the diagnostic OPV trimer band at 416 nm. The UV–vis spectrum of the higher homologue **18** is similar but due to the increased length of the π-conjugated system, the absorption maximum of the OPV moiety is shifted to 461 nm. Preliminary luminescence measurements in CH_2Cl_2 solutions show a strong quenching of the OPV fluorescence by the fullerene moieties in both **16** and **18** indicating the occurrence of intramolecular photoinduced processes. Detailed photophysical studies are

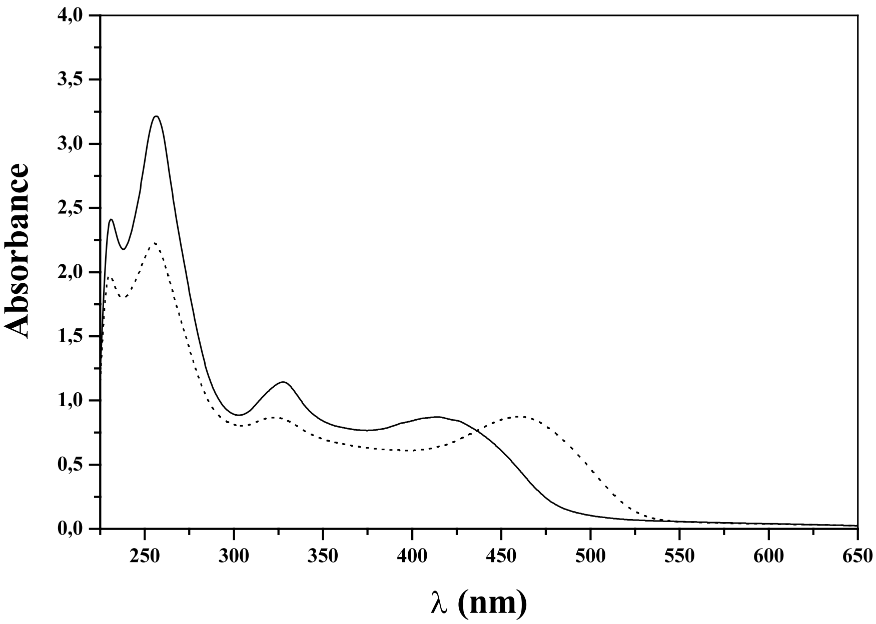


Figure 1. UV–vis spectra of **16** (—) and **18** (·····) in CH_2Cl_2 solutions at room temperature.

currently under investigation in collaboration with the group of Nicola Armaroli (Bologna, Italy) and special emphasis is placed on the detection of photo-induced and long-lived charge-separated states.

In conclusion, an efficient synthesis of symmetrically substituted OPV derivatives has been developed, enabling us to prepare building blocks for the construction of new dumbbell-shaped bis-(pyrazolino-[60]fullerene) OPV derivatives. The electronic properties of these compounds are under investigation and will be reported in due time.

Acknowledgements

This research was supported by the Spanish Ministry of Science and Technology (Project BQU2001-1512, Feder funds and Acción Integrada HF-2001-0016), ECODEV, the French Ministry of Research (*ACI Jeunes Chercheurs*) and the *Picasso* program (Project 04273UE).

References

1. (a) Martín, N.; Sánchez, L.; Illescas, B.; Pérez, I. *Chem. Rev.* **1998**, *98*, 2527–2547; (b) Imahori, H.; Sakata, Y. *Eur. J. Org. Chem.* **1999**, 2445–2457; (c) Gust, D.; Moore, T. A.; Moore, A. L. *Acc. Chem. Res.* **2001**, *34*, 40–48.
2. (a) Effenberger, F.; Grube, G. *Synthesis* **1998**, 1372–1379; (b) Obara, Y.; Takimiya, K.; Aso, Y.; Otsubo, T. *Tetrahedron Lett.* **2001**, *42*, 6877–6881; (c) Liu, S.-H.; Shu, L.; Rivera, J.; Liu, H.; Raimundo, J.-M.; Roncali, J.; Gorgues, A.; Echegoyen, L. *J. Org. Chem.* **1999**, *64*, 4884–4886; (d) Campidelli, S.; Deschenaux, R.; Eckert, J.-F.; Guillon, D.; Nierengarten, J.-F. *Chem. Commun.* **2002**, 656–657; (e) Gu, T.; Nierengarten, J.-F. *Tetrahedron Lett.* **2001**, *42*, 3175–3178.
3. (a) Armaroli, N.; Barigelletti, F.; Ceroni, P.; Eckert, J.-F.; Nicoud, J.-F.; Nierengarten, J.-F. *Chem. Commun.* **2000**, 599–600; (b) Fujitsuka, M.; Ito, O.; Yamashiro, T.; Aso, Y.; Otsubo, T. *J. Phys. Chem. A* **2000**, *104*, 4876–4881; (c) Yamasshiro, T.; Aso, Y.; Otsubo, T.; Tang, H.; Harima, Y.; Yamashita, K. *Chem. Lett.* **1999**, 443–444; (d) Segura, J. L.; Gomez, R.; Martin, N.; Guldi, D. M. *Chem. Commun.* **2000**, 701–702; (e) Apperloo, J. J.; Martineau, C.; van Hal, P. A.; Roncali, J.; Janssen, R. A. J. *J. Phys. Chem. A* **2002**, *106*, 21–31.
4. (a) Nierengarten, J.-F.; Eckert, J.-F.; Nicoud, J.-F.; Ouali, L.; Krasnikov, V.; Hadziioannou, G. *Chem. Commun.* **1999**, 617–618; (b) Eckert, J.-F.; Nicoud, J.-F.; Nierengarten, J.-F.; Liu, S.-G.; Echegoyen, L.; Barigelletti, F.; Armaroli, N.; Ouali, L.; Krasnikov, V.; Hadziioannou, G. *J. Am. Chem. Soc.* **2000**, *122*, 7467–7479; (c) Peeters, E.; van Hal, P. A.; Knol, J.; Brabec, C. J.; Sariciftci, N. S.; Hummelen, J. C.; Janssen, R. A. J. *J. Phys. Chem. B* **2000**, *104*, 10174–10190; (d) Guldi, D. M.; Luo, C.; Swartz, A.; Gomez, R.; Segura, J. L.; Martin, N; Brabec, C.; Sariciftci, N. S. *J. Org. Chem.* **2002**, *67*, 1141–1152; (e) Gu, T.; Tsamouras, D.; Melzer, C.; Krasnikov, V.; Gisselbrecht, J.-P.; Gross, M.; Hadziioannou, G.; Nierengarten, J.-F. *ChemPhysChem* **2002**, 124–127; (f) Armaroli, N.; Accorsi, G.; Gisselbrecht, J.-P.; Gross, M.; Krasnikov, V.; Tsamouras, D.; Hadziioannou, G.; Gomez-Escalonilla, M. J.; Langa, F.; Eckert, J.-F.; Nierengarten, J.-F. *J. Mater. Chem.* **2002**, *12*, 2077–2087.
5. (a) Apperloo, J. J.; Langeveld-Voss, B. M. W.; Knol, J.; Hummelen, J. C.; Janssen, R. A. J. *Adv. Mater.* **2000**, *12*, 908–911; (b) Segura, J. L.; Martin, N. *Tetrahedron Lett.* **1999**, *40*, 3239–3242; (c) Martineau, C.; Blanchard, P.; Rondeau, D.; Delaunay, J.; Roncali, J. *Adv. Mater.* **2002**, *14*, 283–287.
6. (a) de la Cruz, P.; Díaz-Ortiz, A.; García, J. J.; Gómez-Escalonilla, M. J.; de la Hoz, A.; Langa, F. *Tetrahedron*

Lett. **1999**, *40*, 1587–1590; (b) Langa, F.; de la Cruz, P.; Espíldora, E.; de la Hoz, A.; Bourdelande, J. L.; Sánchez, L.; Martín, N. *J. Org. Chem.* **2001**, *66*, 5033–5041; (c) Langa, F.; Gómez-Escalonilla, M. J.; Diez-Barra, E.; García-Martinez, J. C.; de la Hoz, A.; Rodríguez-López, J.; González-Cortés, A.; López-Arza, V. *Tetrahedron Lett.* **2001**, *42*, 3435–3438; (d) Langa, F.; de la Cruz, P.; Delgado, J. L.; Gómez-Escalonilla, M. J.; González-Cortés, A.; de la Hoz, A.; López-Arza, V. *New. J. Chem.* **2002**, *26*, 76–80; (e) Espíldora, E.; Delgado, J. L.; de la Cruz, P.; de la Hoz, A.; López-Arza, V.; Langa, F. *Tetrahedron* **2002**, *58*, 5821–5826.

7. Müllen, K.; Wegner, G. *Electronic Materials*: *the Oligomer Approach*; Wiley-VCH: Weinheim, 1998.
8. Selected spectroscopic data for **16**: ^{1}H NMR (CDCl$_3$) δ 8.34 (d, J=9.5 Hz, 4H), 8.26 (d, J=9.5 Hz, 4H), 7.57 (B of AB, J=17 Hz, d, 2H), 7.48 (A of AB, J=17 Hz, d, 2H), 7.28 (s, 2H), 7.21 (s, 2H), 7.14 (s, 2H), 4.05–3.99 (m, 12H), 1.90–1.71 (m, 12H), 1.57–1.25 (m, 60H), 0.96–0.75 (m, 18H); ^{13}C NMR (CDCl$_3$): δ 151.9, 151.0, 150.3, 150.0, 147.6, 147.0, 146.9, 146.6, 146.2, 146.1, 145.9, 145.8, 145.5, 145.3, 145.2, 145.1, 144.6, 144.3, 143.9, 143.1, 142.8, 142.7, 142.3, 142.1, 141.9 (2C), 141.8, 140.6, 139.2, 137.1, 135.0, 130.3, 127.2, 125.3, 123.1, 119.1, 119.0, 116.3, 110.7, 89.3, 84.3, 69.9, 69.5, 32.2, 30.0, 29.9, 29.8, 29.7, 26.7, 26.6, 26.5, 23.0, 14.5, 14.4; IR (KBr): ν 2925.4, 1638.6, 1616.7, 1587.6 (CH=N), 1493.0, 1328.1, 1197.1, 1022.5, 845.4, 527.7; UV–vis (CH$_2$Cl$_2$) λ_{max}/nm (log ε) 416 (5.0), 327 (5.1), 257 (5.5); MALDI-TOF m/z 2812.7 (M$^+$, calcd for $C_{204}H_{120}N_6O_{10}$: 2812.90). **17**: ^{1}H NMR (CDCl$_3$) δ 10.4 (s, CHO, 1H), 8.32 (d, J=9.5 Hz, 2H), 8.24 (d, J=9.5 Hz, 2H), 7.55–7.44 (m, 4H), 7.26 (s, 2H), 7.20 (s, 2H), 7.13 (s, 2H), 4.05–4.02 (m, 12H), 1.86–1.71 (m, 12H), 1.58–1.25 (m, 60H), 0.88–0.79 (m, 18H). IR (KBr): ν 2852.5, 1733.0 (C=O), 1677.4, 1591.9 (CH=N), 1467.9, 1322.6, 1198.6, 852.3, 526.9; UV–vis (CH$_2$Cl$_2$) λ_{max}/nm (log ε) 420 (4.7), 325 (4.8), 255 (5.2), 231 (5.1); MALDI-TOF m/z 1959.8 (M$^+$, calcd for $C_{138}H_{117}N_3O_9$: 1959.87). **18**: ^{1}H NMR (CDCl$_3$) δ 8.34 (d, J=9.5 Hz, 4H), 8.26 (d, J=9.5 Hz, 4H), 7.58 (B of AB, J=17 Hz, d, 4H), 7.48 (A of AB, J=17 Hz, d, 4H), 7.29 (s, 2H), 7.28 (s, 2H), 7.21 (s, 2H), 7.17 (s, 2H), 7.15 (s, 2H), 4.10–4.00 (m, 20H), 1.92–1.82 (m, 20H), 1.58–1.27 (m, 100H), 0.89–0.81 (m, 30H); ^{13}C NMR (CDCl$_3$): δ 151.9, 150.9, 150.1, 147.6, 147.0, 146.3, 146.1, 146.0, 145.8, 145.5, 145.2, 145.1, 144.7, 144.3, 143.1, 142.9, 142.3, 142.2, 142.0, 140.7, 139.2, 137.1, 135.2, 130.4, 127.9, 126.8, 125.4, 123.3, 114.2, 110.5, 97.8, 89.3, 83.5, 69.9, 69.5, 32.2, 29.8, 29.7, 26.6, 26.5, 23.8, 23.0, 14.5, 14.4; IR (KBr): ν 2921.3, 1636.3, 1616.5, 1588.1 (CH=N), 1495.5, 1319.9, 1262.9, 1020.9, 800.2, 527.3; UV–vis (CH$_2$Cl$_2$) λ_{max}/nm (log ε) 461 (4.2), 324 (4.2), 255 (4.7), 230 (4.6); MALDI-TOF m/z 3529.8 (M$^+$, calcd for $C_{252}H_{196}N_6O_{14}$: 3529.48). **19**: ^{1}H NMR (CDCl$_3$) δ 10.4 (s, CHO, 1H), 8.32 (d, J=9.5 Hz, 2H), 8.26 (d, J=9.5 Hz, 2H), 7.66–7.44 (m, 8H), 7.33 (s, 2H), 7.21 (s, 2H), 7.18 (s, 2H), 7.17 (s, 2H), 7.15 (s, 2H), 4.07–4.04 (m, 20H), 1.89–1.86 (m, 20H), 1.59–1.27 (m, 100H), 0.90–0.85 (m, 30H). IR (KBr): ν 2925.3, 2850.4, 1717.3 (C=O), 1636.7, 1618.5, 1587.3 (CH=N), 1496.3, 1322.1, 1257.1, 1197.3, 802.1, 526.6; UV–vis (CH$_2$Cl$_2$) λ_{max}/nm (log ε) 467 (4.0), 323 (3.9), 255 (4.3), 230 (4.2); MALDI-TOF m/z 2676.5 (M$^+$, calcd for $C_{186}H_{193}N_3O_{13}$: 2676.45).