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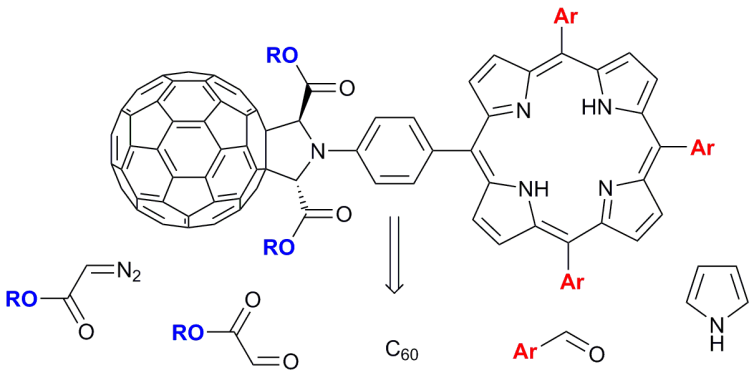

Triaryl-substituted pyrrolo-*p*-phenylene-linked porphyrin-fullerene dyads: expanding the structural diversity of photoactive materials

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Abstract

A protocol for the synthesis of pyrrolo-*p*-phenylene-linked porphyrin-fullerene dyads suitable as photoactive materials was developed. The sequence of aziridination – aziridine ring opening – 1,3-dipolar cycloaddition reactions enabled us to provide structural variability both to the porphyrin core and to pyrrole linker, which facilitates designing the electronic structure and morphological parameters of the dyads. The key porphyrin building blocks, nitro-porphyrins, were synthesized by a stochastic cyclocondensation of arenecarbaldehydes with *p*-nitrophenyl(dipyrrolyl)methane.

Keywords: dipolar cycloaddition; aziridines; donor-acceptor conjugates; fullerenes; porphyrins

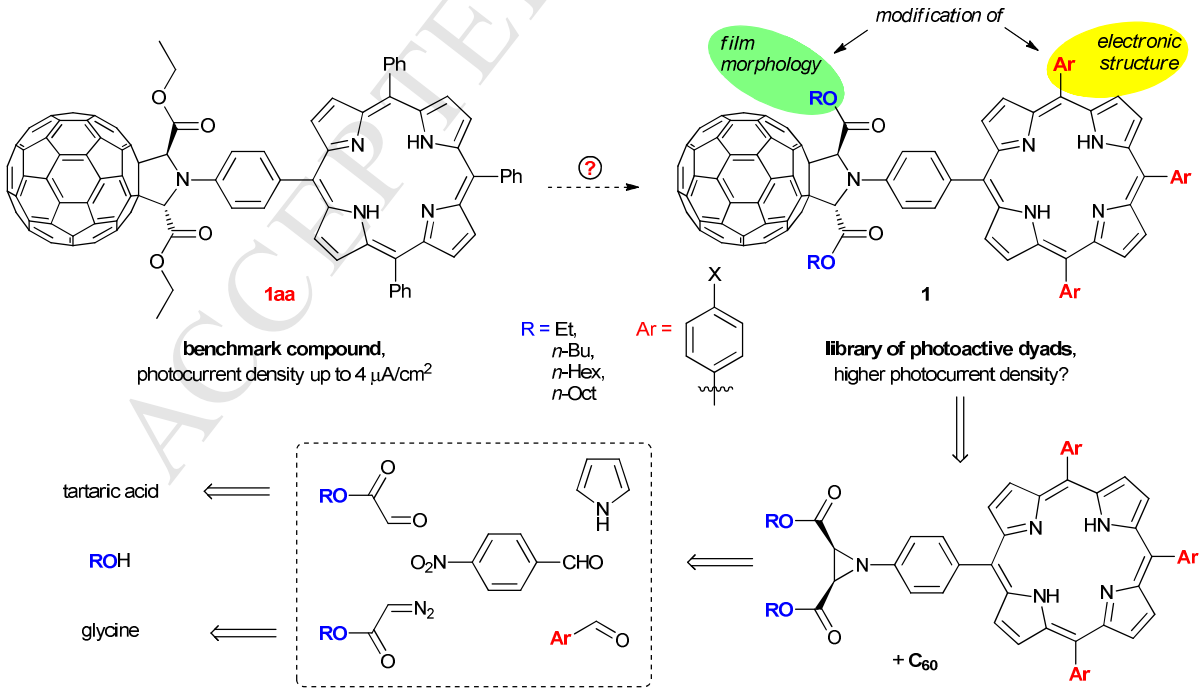
Introduction

Porphyrin-fullerene dyads can form a charge separated (CS) state through the intramolecular electron transfer processes upon photoexcitation,[1-4] and have been considered as promising candidates for the materials for photovoltaic[5,6] or photo-redox-catalytic applications.[6-8] Recently, Buldum and Reneker predicted that a rigid *p*-phenylene linked donor-acceptor dyad should secure dual-channel film morphology favoring the charge transport after the initial step of the charge separation.[9] In our recent work, we demonstrated a photovoltaic activity of a similar *p*-phenylene linked porphyrin-fullerene dyad **1aa** which exhibited the photocurrent of up to 4 $\mu A \cdot cm^{-2}$.[10]

The performance of the photovoltaic devices based on compounds of this class of dyads should depend on the electronic and morphological parameters on the molecular level. The most straightforward route for

the tuning the electronic structure of the porphyrin-fullerene dyad is to vary the substituents at the porphyrin core, which should affect the Gibbs free energy for the charge recombination and the electronic coupling between the donor and acceptor moieties, both of which are the important parameters in Marcus theory of charge transfer. Within the class of the dyads, the simplest representative of which is compound **1aa**, the morphology of the photoactive films made from such porphyrin-fullerene dyads is expected to be varied by the changes in the alkyl chains in the ester fragments because of the associated changes in the intermolecular interactions between the dyads as well as in their steric sizes.

In the present study, we focus on the series of porphyrin-fullerene dyads **1** bearing various substituents in *p*-position of *meso*-phenyl rings (Scheme 1), including strong π-donor (CH_3O), weak σ-donor (CH_3), π-donor and σ-acceptor (Br) along with strong σ-acceptor (CF_3), and alkyl groups of various lengths in the ester fragments containing ethyl, *n*-butyl, *n*-hexyl and *n*-octyl groups, and develop our synthetic methodology for the preparation of pyrrolo-*p*-phenylene-linked porphyrin-fullerene dyads so that the structural parameters responsible for the perturbation of the electronic structure of the dyad as well as for the morphology of the film composed of the dyads can be manipulated. In the course of the exploration of the synthetic routes, we found that nitro-porphyrins are convenient building blocks to incorporate variable aryl groups into the porphyrin-fullerene dyads.



Scheme 1. Synthetic target: the library of photoactive porphyrin-fullerene dyads **1**.

Results and discussion

Taking into account the theoretical work of Buldum and our experimental results on the photocurrent induced by dyad **1aa**, we selected the co-axial orientation of the donor and acceptor fragments (tetraarylporphyrin and pyrrolofullerene respectively) to be the key structural parameter to be achieved in the synthesis of a photoactive donor-acceptor dyad. This can be implemented by constructing the pyrrolidine ring of the pyrrolofullerene fragment *via* 1,3-dipolar cycloaddition of suitable azomethine-ylides across [6,6]-double bond of fullerene C_{60}, which is known as Prato reaction.[11]

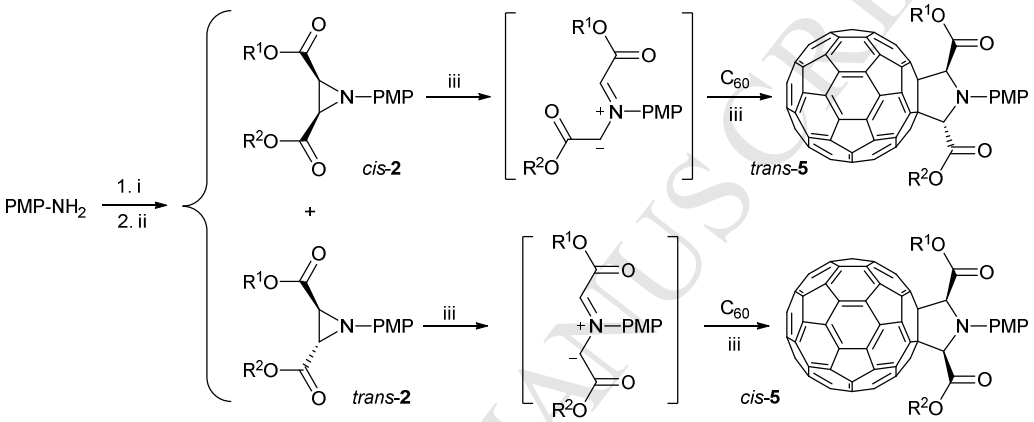
Azomethine-ylides are usually highly reactive intermediates, which cannot be isolated in most cases and need to be generated *in situ*. In Prato reaction, azomethine-ylides are commonly generated by (i) condensation of α-amino acids with aldehydes or ketones;[12] (ii) prototropic isomerization of imines[13] and (iii) electrocyclic ring-opening of aziridines.[14] Among these methods, the last approach suits best our synthetic goal. The potential advantages of the aziridine-based method for azomethine-ylide generation include stereospecificity of the ylide formation, the easy synthetic route towards the ylide precursor and the simplicity of introducing structural variations in the target dyads, as can be seen from the retrosynthetic disconnection of the target class of compounds down to commercial chemicals (Scheme 1).

The main synthetic problems to be solved for practical implementation of this route include the synthesis of unsymmetric A_3B-type porphyrin synthetic block, the construction of the aziridine ring bearing various alkoxycarbonyl groups and the verification of applicability of the synthesized set of porphyrinylaziridines in Prato reaction with fullerene C_{60}.

First, the variability of the alkoxycarbonyl groups in the key step of the dyad synthesis, in which the 1,3-cycloaddition of azomethine ylides across C=C bond of C_{60}, was tested on a model reaction series of fullerene C_{60} with dialkyl *N*-(*p*-methoxyphehyl)aziridine dicarboxylates **2**.

Aziridines **2** were obtained (Scheme 2) by condensation of *p*-methoxyaniline with alkylglyoxylate **3**, accessible by oxidative cleavage of dialkyl tartrates with periodic acid, followed by BF_3-catalyzed aziridination with alkyl diazoacetate **4**, accessible from alkyl glycinate. The reaction proceeded smoothly for various combinations of alkyl substituents in the starting imine and the diazocompound yielding mixtures of *cis*- and *trans*-aziridines **2** in 79 – 99% yield (Table 1). In accord with the previous reports on aziridination reactions,[15] *cis*-aziridines were the major products with the ratio of *cis*/*trans* aziridines in the range between 5:1 and 12:1.

Unsymmetrically substituted *trans*-aziridines *trans*-**2ab**, *trans*-**6ac** and *trans*-**2ad** showed expectable AB pattern at 3.44 ppm for the aziridine protons with $^3J_{HH}$ coupling constant of 2 Hz, typical for *trans*-aziridines.[16] The corresponding AB signal for *cis*-aziridines *cis*-**2ab**, *cis*-**2ac**, *cis*-**2ad** was reduced to a singlet shifted to the stronger field (3.0 ppm). Configuration of these aziridines and of symmetrically substituted aziridines **2aa**, **2bb**, **2cc** and **2dd** was confirmed by observing the $^3J_{HH}$ coupling of the ^{13}C-satellite signals. *Cis*-aziridines are characterized by $^3J_{HH}$ of 6-7 Hz,[17] while *trans*-aziridines show lesser value of 0-2 Hz (Table 1).



i. R^1O_2CCHO (**3**), C_6H_6, rt; ii. $R^2O_2CCHN_2$ (**4**), BF_3*OEt_2, Et_2O, rt; iii. 100 °C, ^{o}DCB

R^1,R^2 = Et **(a)**, *n*-Bu **(b)**, *n*-Hex **(c)**, *n*-Oct **(d)**

Scheme 2. Synthesis of pyrrolofullerenes.

Table 1. Reaction yields and selected NMR data for aziridines **2**.

2	R^1	R^2	Yield of *cis*-**2**, %	Yield of *trans*-**2**, %	$^3J_{HH}$, Hz *cis*-**2**	δ $H^{2(3)}$, ppm c*is*-**2**	$^3J_{HH}$, Hz *trans*-**2**	δ $H^{2(3)}$, ppm *trans*-**2**
2aa [18]	Et	Et	86	13	6[a]	3.04	0[a]	3.44
2ab	Et	Bu	77	14	6.7[a]	3.00	2.4	3.43, 3.44
2ac	Et	Hex	78	12	6.7[a]	3.03	2.4	3.43, 3.44
2ad	Et	Oct	73	6	6.7[a]	3.03	2.3	3.43, 3.44
2bb	Bu	Bu	82	17	6.7[a]	3.03	2.4[a]	3.43
2cc	Hex	Hex	86	10	6.6[a]	3.02	2.4[a]	3.45
2dd[18]	Oct	Oct	81	13	6[a]	3.04	0[a]	3.44

[a]For ^{13}C satellite signals.

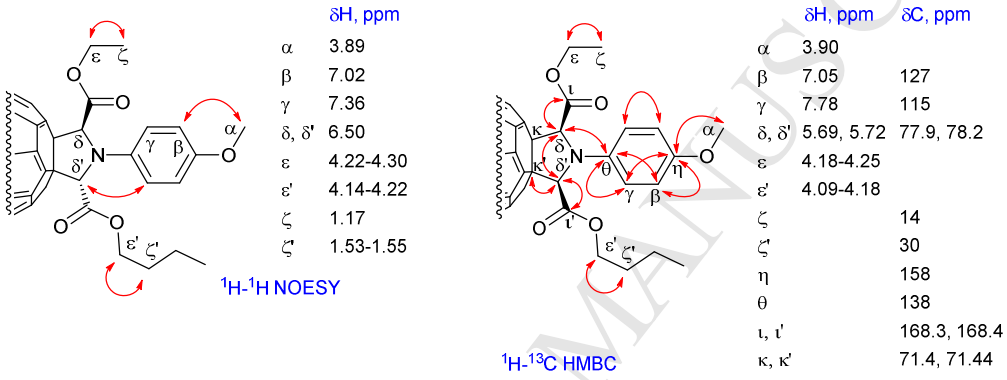
Table 2. Reaction yields and selected NMR data for fulleropyrrolidines **5**.

5	R^1	R^2	*Trans*				*Cis*			
			Yield, %	$\delta H^{2(5)}$, ppm	$\delta C^{2(5)}$, ppm	$\delta C^{3(4)}$, ppm	Yield, %	$\delta H^{2(5)}$, ppm	$\delta C^{2(5)}$, ppm	$\delta C^{3(4)}$, ppm
5aa[18]	Et	Et	47	6.51	74.7	71.2	-	-	-	-
5ab	Et	Bu	49	6.50	74.6, 74.9	71.2, 71.23	48	5.69, 5.72	77.9, 78.2	71.4, 71.44
5ac	Et	Hex	57	6.50, 6.51	74.6, 74.9	71.21, 71.24	59	5.70, 5.72	77.9, 78.1	71.38, 71.43
5ad	Et	Oct	38	6.50	74.6, 74.9	71.22, 71.24	42	5.70, 5.72	77.9, 78.1	71.40, 71.44
5bb	Bu	Bu	57	6.51	74.8	71.3	25	5.71	78.2	71.4
5cc	Hex	Hex	50	6.51	74.8	71.2	58	5.71	78.1	71.4
5dd[18]	Oct	Oct	41	6.52	74.8	71.2	31	5.72	78.1	71.4

Aziridines **2** were reacted with fullerene C_{60} to give pyrrolofullerenes **5** (Scheme 2) in 25 – 59% yield (Table 2). The solubility of the resulting adducts increased dramatically when either one or both ethyl groups in **5aa** were changed for longer alkyl chains: *n*-butyl, *n*-hexyl or *n*-octyl. The reaction of aziridines **2** with C_{60} proceeded stereospecifically, with *cis*-aziridines giving only *trans*-adducts, and *trans*-aziridines – *cis*-adducts.

The configuration of the pyrrolofullerenes was established based on the chemical shift of the pyrrolidine $HC^{2(5)}$ proton in ^1H NMR spectra. The signal of this proton is shifted towards weak field for *trans*-pyrrolofullerenes as compared to *cis*-pyrrolofullerenes[18] (6.5 and 5.7 ppm respectively). For unsymmetrically substituted pyrrolofullerenes **5ab**, **5ac** and **5ad**, the signals of the pair of non-equivalent pyrrolidine protons H^2 and H^5 could be discerned as two singlets both for cis-isomers (5.69 and 5.71 ppm) and trans-isomers (6.50 and 6.51), except compound *trans*-**5ab**, where the corresponding signals coalesced into a single singlet (6.5 ppm) of double integral intensity. We attribute this to the strong deshielding effect of the carbonyl group in the case of trans-isomers, which masks the small differences in

chemical surrounding of these protons. The non-equivalence of the CH fragments in the pyrrolidine ring can be seen in ^{13}C NMR spectra of this pyrrolofullerene, where a pair of signals for $C^{2(5)}$ carbons was observed (74.6 and 74.9 ppm for trans-isomers) along with two more signals for $C^{3(4)}$ carbons (71.20, 71.23) (Table 2). The attribution of signals for $C^{2(5)}$ and $C^{3(4)}$ carbons was based on the correlation cross-peaks observed in ^{1}H-^{13}C HSQC spectrum of *cis*-**5ab** between the pyrrolidine protons signals at 5.7 ppm and the $C^{2(5)}$ carbons signals at 78 ppm due to the $^{1}J_{C\text{-}H}$ heterocoupling constant combined with the observation of the intensive correlation cross-peaks in ^{1}H-^{13}C HMBC spectrum of *cis*-**5ab** between the pyrrolidine protons signals at 5.7 ppm and the $C^{3(4)}$ carbons signals at 71.4 ppm, which was due to the $^{3}J_{C\text{-}H}$ vicinal heterocoupling constant (Scheme 3).

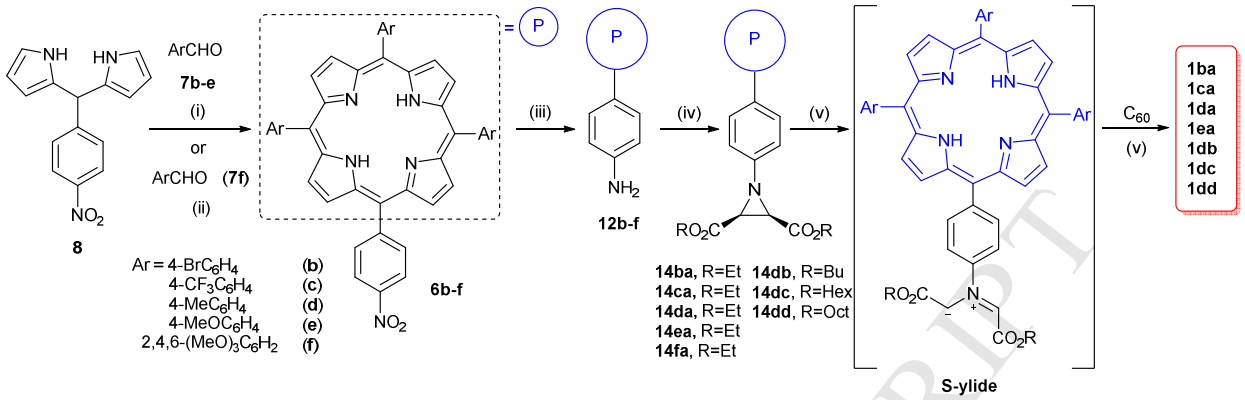


Scheme 3. Representation of cross-peaks in 2D NMR spectra of *trans*-**5ab** and *cis*-**5ab**.

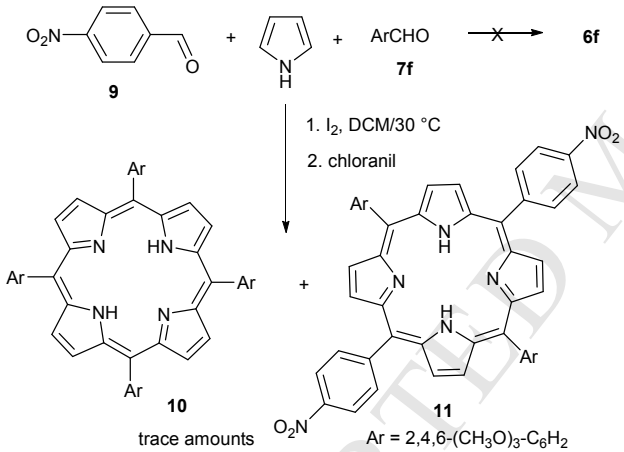
The protocol for construction of an aziridine ring on a porphyrin framework has been reported in our previous work[10] for compound **1aa**. However, a different approach to the synthesis of the key intermediates, nitro-porphyrins **6b-f**, was found to be necessary in the case of dyads bearing substituted aryl group. To synthesize these porphyrins, a stochastic cyclocondensation of arenecarbaldehydes **7b-f** with *p*-nitrophenyl(dipyrrolyl)methane **(8)** was used instead of nitration of the corresponding unsymmetrical porphyrins (Scheme 4).

Compared to the reaction with *p*-nitrobenzaldehyde, the application of dipyrromethane **8** reduces the differences in reactivity of different aldehydes, providing kinetic uniformity, which is important for successful formation of A_3B porphyrinogens in a stochastic cyclocondensation step. Otherwise, when aldehydes A and B of significantly different reactivity are directly condensed with pyrrole, formation of A_4 or B_4 porphyrins prevails. For example, reaction of aldehyde **7f** containing extremely electron-rich 2,4,6-trimethoxysubstituted phenyl ring with electron-deficient *p*-nitrobenzaldehyde **(9)** and pyrrole gave mainly symmetric porphyrins **10** and **11** (Scheme 5), whereas the replacement of aldehyde **9** with

dipyrromethane **8** resulted in the successful synthesis of mixed A_3B-type nitro-porphyrin **6f** in 12% yield (Scheme 4).



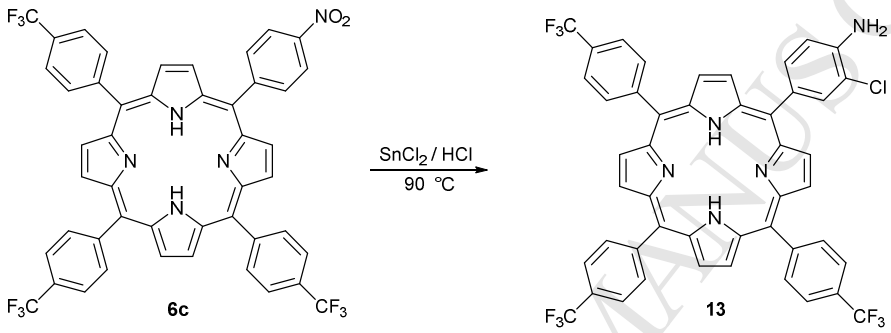
Scheme 4. Synthesis of target porphyrin-fullerene dyads **1**. Reaction conditions: i. 1. Pyrrole, I_2, DCM/30 °C, 2. chloranil; ii. 1. Pyrrole, I_2, $CHCl_3$/61 °C 2. chloranil; iii. 1. $SnCl_2$/HCl, 2. NH_4OH aq.; iv. 1. RO_2CCHO, 2. RO_2CCHN_2, $BF_3 \cdot OEt_2$; v. chlorobenzene/100 °C.



Scheme 5. Side-reactions in stochastic condensation of aldehydes **9** and **7f** with pyrrole.

Nitro-porphyrins **6b-f** were reduced to amino-porphyrins **12b-f** by $SnCl_2$[19,20,21] in hydrochloric acid. Alternative reports suggest reduction by $NaBH_4$/Pd/C,[22] or H_2/Pd,[23] but tin(II) chloride seems to be the most common reductant. In our systems, the reduction proceeded smoothly giving the desired amino-porphyrins in 47-84% yield (Scheme 4) in most cases. However, when strong acceptors like CF_3-group were presented in the tetraphenylporphyrin central core, the reduction proceeded with a low conversion (yet with good yield, 67% yield of reduction step as estimated for a two-step synthesis of **12c** from **6c**) and attempts were made to accelerate it by applying more harsh conditions of elevated temperature. In this case, the conversion of the starting material was complete but the yield of **12c** decreased to 26% and the reaction was accompanied by chlorination of the *p*-nitrophenyl group, giving after *in situ* reduction

chlorinated amino-porphyrin **13** as a by-product in 29% yield (Scheme 6). No chlorination product was observed when amino-porphyrin **12c** was subjected to the identical reaction conditions, confirming that chlorination proceeds before the reduction step. ^{1}H NMR spectra of **13** showed multiplets pattern typical for 1,2,4-trisubstituted phenyl rings as AB system doublet at 7.14 and at 8.12 ppm along with the doublet of doublets at 7.92 ppm. 2D NOESY NMR spectrum showed correlation of β-pyrrolic protons of the porphyrin fragment with the protons of 1,2,4-trisubstituted benzene ring as two cross-peaks (8.78 vs 7.92 ppm and 8.78 vs. 8.12 ppm), unequivocally demonstrating that the chlorination proceeded in ortho-position with respect to nitro group. Alternative position for chlorination would result in only one cross-peak of the protons of pyrrole and benzene rings.



Scheme 6. Chlorination-reduction of porphyrin **6c**.

Condensation of the amino-porphyrins **12b-f** with alkyl glyoxylates **3a-d** followed by Lewis-acid catalyzed nucleophilic addition of alkyl diazoacetates **4a-d** gave aziridinyl-porphyrins **14** in 49-83% yields. Aziridination of **6f** was not successful as the reaction was accompanied by partial removal of methoxy-groups, leading to very low yield (9%) of the target aziridine **14fa**. In all cases (other than compound **14fa**), the reaction proceeded smoothly to selectively give *cis*-aziridines, in accord with the previous reports on $BF_3 \cdot Et_2O$ catalyzed reaction of imines with diazo compounds.[15,18]

Configuration of the aziridine ring was established based on the values of vicinal spin-spin coupling constant on ^{13}C-2-satellite doublets[24] of the aziridine protons, which comprised 6.9 Hz, typical for *cis*-aziridines (6-7 Hz[17] *vs.* 0-3 Hz[16] in *trans*-aziridines). Independent confirmation of aziridine *cis*-configuration was obtained in the case of reaction with amino-porphyrins **12c** (CF_3) and **12e** (CH_3O), where *trans*-aziridines ***trans*-14ca**,**ea** were isolated in 10-12% yield and characterized by ^{1}H-NMR. Comparison of ^{1}H-NMR spectra of ***cis*-** and ***trans*-14ca**,**ea** shows that the signal of the aziridine protons is shifted downfield in ***trans*-14ca**,**ea** compared to the same signal in ***cis*-14ca**,**ea** (3.8 *vs.* 3.5 ppm). This

downfield shift for *trans*-aziridines has been known well[24] and it can be ascribed to deshielding effect of the ester carbonyl group. All other aziridines ***cis*-14** show chemical shift of 3.4-3.5 ppm for the aziridine protons, independently confirming the assignment of the aziridine configurations.

Aziridinyl-porphyrines **14** were reacted with fullerene C_{60} to give the target porphyrin-fullerene dyads **1** in 21-48% yield (Scheme 4). The reaction proceeded stereoselectively and gave exclusively *trans*-adducts in accord with Woodward-Hoffman's rules for the sequence of concerted processes: *cis*-aziridine ring-opening to *S*-ylide followed by cycloaddition across C=C bond between two six-membered rings in fullerene C_{60} forming the *trans*-pyrrolidine ring condensed to C_{60} skeleton.

HRMS data on the dyads were consistent with the proposed brutto-formulae. ^{1}H NMR spectra showed characteristic signals of fulleropyrrolidine fragment (singlet at ca. 6.7 ppm for C<u>H</u>CO_2R) along with characteristic signals of the porphyrin fragment (strong-field singlet for NH protons at ca. -2.7 − -2.8 ppm and weak-field two AB systems at 8.8-9.0 ppm for β-pyrrolic protons). ^{13}C NMR spectra showed characteristic signals for the pyrrolidine ring carbons at 71 and 75 ppm along with broad singlet at 130-131 ppm typical for β-pyrrolic carbons of the porphyrin ring. The configuration of the adducts was established on the basis of chemical shift for the pyrrolidine protons (6.7-6.8 ppm).[10,24,25]

Steady-state absorption and emission measurements showed spectroscopic features characteristic of porphyrin compounds[26] (Fig. S133, Supporting information): absorption spectra of benzonitrile solution of dyads **1** showed a strong band at ca. 425 nm (Soret band) and four bands of much smaller intensities in the range of 480-680 nm (refered to as Q-bands:[27] ca. 520, 555, 595 and 650 nm).

A comparison of the UV/Vis spectra of the dyads with the spectra of porphyrinyl aziridines **14** and fulleropyrrolidines **5** shows that only a weak coupling of porphyrin and fullerene chromophores occurs in the dyads because the absorption spectra of dyads **1** are roughly a superposition of the absorption spectra of two separate chromophores in compounds **14** and **5**. The UV/Vis spectra for compounds **1da**, **14da** and **5aa** are presented on Fig. 1 as a typical example.

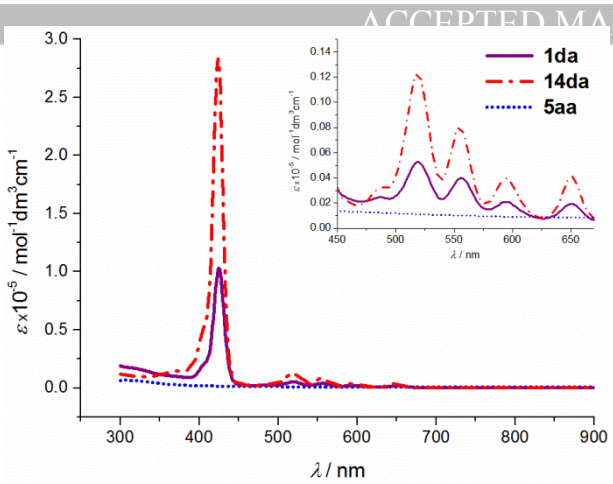


Figure 1. UV/Vis absorption spectra of dyad **1da,** porphyrin **14da** and pyrrolofullerene **5aa** in PhCN.

The emission spectra of dyads **1** showed emission peaks at ca. 656 and 724 nm (Fig. S135). The observed fluorescence lifetime was ca. 1-3 ns, with the fluorescence quantum yield of less than 1%.

Conclusions

The synthetic protocol based on the incorporation of an aziridine pendant to porphyrin ring has been demonstrated to afford structural diversity in the synthesis of porphyrin-fullerene dyads necessary in the optimization of the molecular structures of this class of photoactive material. It has been shown that both porphyrin and fulleropyrrolidine moieties can be modified by this synthetic approach, which allows us to optimize the electronic properties of the porphyrin-fullerene donor acceptor system and design the morphology of the material formed by these dyads through the modification of the intermolecular interactions via a variability of the solubilizing alkyl ester group.

Experimental section

General. IR spectra were recorded on an FTIR-8400S Shimadzu spectrometer. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were determined in $CDCl_3$ on Bruker 400 spectrometer. Chemical shifts (δ) are reported in ppm downfield from Me_4Si. HRMS was performed using a Bruker MaXis Q-TOF mass spectrometer. Flash chromatography was performed on silica Merck 60.

Starting materials and known compounds. Commercial solvents were purified according to standard techniques. Alkyl glyoxilates **3**,[28] alkyl diazoacetates **4**,[29,30] *p*-nitrophenyldipyrrometane **(8)**,[31] 1,3,5-

trimethoxybenzaldehyde **7f**,[32] 4-(trifluoromethyl)benzaldehyde **7c**[33] were obtained according to published procedures.

General procedure for the synthesis of aziridines 2. A mixture of 4-methoxyaniline (1 eq), alkyl glyoxylate **3** (1.5 eq) and anhydrous Na_2SO_4 (100 mg) in dry benzene (2 ml) was stirred at ambient temperature for 30-40 min. Sodium sulfate was filtered off and the solvent was removed *in vacuo*. The residue was dissolved in dry ether (8 ml) and 1-2 droplets of boron trifluoride etherate were added. A solution of alkyl diazoacetate **4** (1.1 eq) in dry ether (2 ml) was added dropwise and the mixture was stirred for another 2 h and quenched with 5 droplets of triethylamine. The mixture was diluted with water, extracted with DCM and dried over Na_2SO_4. The desiccant was filtered off, the solvent was removed *in vacuo* and the residue was separated by column chromatography (silica gel, petroleum ether – ethyl acetate) to afford products as yellowish oils.

***O*-Ethyl-*O*-butyl *cis*-1-(4-methoxyphenyl)aziridine-2,3-dicarboxylate (*cis*-2ab).** Yield: 77% (247 mg, 0.77 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz): δ=0.94 (t, ^3J(H,H)=7.4 Hz, 3H; C$\underline{H}_3$CH$_2$C), 1.31 (t, ^3J(H,H)=7.2 Hz, 3H; C$\underline{H}_3$CH$_2$O), 1.34–1.45 (m, 2H; CH$_3$C$\underline{H}_2$C), 1.62–1.71 (m, 2H; C$\underline{H}_2$CH$_2$O), 3.00 (s, 2H; HC$_{az}$), 3.74 (s, 3H; CH$_3$O), 4.20 (t, ^3J(H,H)=6.7 Hz, 2H; CH$_2$C$\underline{H}_2$O), 4.26 (q, ^3J(H,H)=7.2 Hz, 2H; CH$_3$C$\underline{H}_2$O), 6.78 (AA'BB', ^3J(H,H)=8.9 Hz, 2H; OC=CH), 6.94 (AA'BB', ^3J(H,H)=8.9 Hz, 2H; NC=CH); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=13.6 (C$\underline{H}_3$CH$_2$C), 14.0 (C$\underline{H}_3$CH$_2$O), 18.9 (CH$_3$C$\underline{H}_2$C), 30.4 (C$\underline{H}_2$CH$_2$O), 43.1 (C$_{az}$), 43.2 (C$_{az}$), 55.4 (CH$_3$O), 61.7 (CH$_3$C$\underline{H}_2$O), 65.5 (CH$_2$C$\underline{H}_2$O), 114.3 (OC=C$\underline{H}$), 120.8 (NC=C$\underline{H}$), 144.2 (NC=CH), 156.2 (OC=CH), 166.96 (C=O), 167.01 (C=O); IR (KBr): $\tilde{\nu}$=1734, 1754 (C=O); HRMS (ESI): *m*/*z*: calcd for $C_{17}H_{23}NO_5Na^+$, 344.1468 $[M+Na]^+$; found 344.1484.

***O*-Ethyl-*O*-butyl *trans*-1-(4-methoxyphenyl)aziridine-2,3-dicarboxylate (*trans*-2ab).** Yield: 14% (44 mg, 0.14 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz): δ=0.92 (t, ^3J(H,H)=7.4 Hz, 3H; C$\underline{H}_3$CH$_2$C), 1.24 (t, ^3J(H,H)=7.1 Hz, 3H; C$\underline{H}_3$CH$_2$O), 1.29–1.36 (m, 2H; CH$_3$C$\underline{H}_2$C), 1.52–1.59 (m, 2H; C$\underline{H}_2$CH$_2$O), 3.43 (AB, ^3J(H,H)=2.4 Hz, 1H; HC$_{az}$), 3.44 (AB, ^3J(H,H)=2.4 Hz, 1H; HC$_{az}$), 3.76 (s, 3H; CH$_3$O), 4.04–4.14 (m, 2H; CH$_2$C$\underline{H}_2$O), 4.15–4.21 (m, 2H; CH$_3$C$\underline{H}_2$O), 6.78 (AA'BB', ^3J(H,H)=9.0 Hz, 2H; OC=CH), 6.84 (AA'BB', ^3J(H,H)=9.0 Hz, 2H; NC=CH); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=13.6 (C$\underline{H}_3$CH$_2$C), 14.0 (C$\underline{H}_3$CH$_2$O), 18.9 (CH$_3$C$\underline{H}_2$C), 30.4 (C$\underline{H}_2$CH$_2$O), 42.3 (C$_{az}$), 42.4 (C$_{az}$), 55.4 (CH$_3$O), 61.7 (CH$_3$C$\underline{H}_2$O), 65.6 (CH$_2$C$\underline{H}_2$O), 114.2 (OC=C$\underline{H}$), 120.6 (NC=C$\underline{H}$), 140.4 (NC=CH), 155.9 (OC=CH), 167.0 (C=O),

167.1 (C=O); IR (KBr): $\tilde{\nu}$=1738 (C=O); HRMS (ESI): *m*/*z*: calcd for $C_{17}H_{23}NO_5Na^+$, 344.1468 $[M+Na]^+$; found 344.1477.

***O*-Ethyl-*O*-hexyl *cis*-1-(4-methoxyphenyl)aziridine-2,3-dicarboxylate (*cis*-2ac).** Yield: 78% (273 mg, 0.78 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz): δ=0.91 (t, ^3J(H,H)=7.0 Hz, 3H; C$\underline{H}_3$CH$_2$C), 1.33 (t, ^3J(H,H)=7.2 Hz, 3H; C$\underline{H}_3$CH$_2$O), 1.30–1.42 (m, 6H; CH$_3$(C$\underline{H}_2$)$_3$), 1.65–1.74 (m, 2H; C$\underline{H}_2$CH$_2$O), 3.03 (s, 2H; HC$_{az}$), 3.77 (s, 3H; CH$_3$O), 4.22 (t, ^3J(H,H)=7.0 Hz, 2H; CH$_2$C$\underline{H}_2$O), 4.24–4.33 (m, 2H; CH$_3$C$\underline{H}_2$O), 6.80 (AA'BB', ^3J(H,H)=9.0 Hz, 2H; OC=CH), 6.97 (AA'BB', ^3J(H,H)=9.0 Hz, 2H; NC=CH); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=13.9 (C$\underline{H}_3$CH$_2$C), 14.1 (C$\underline{H}_3$CH$_2$O), 22.5 (CH$_3$C$\underline{H}_2$C), 25.4 (CH$_3$CH$_2$C$\underline{H}_2$), 28.4 (CH$_3$(CH$_2$)$_2$C$\underline{H}_2$), 31.3 (C$\underline{H}_2$CH$_2$O), 42.2 (C$_{az}$), 42.3 (C$_{az}$), 55.4 (CH$_3$O), 61.7 (CH$_3$C$\underline{H}_2$O), 65.9 (CH$_2$C$\underline{H}_2$O), 114.4 (OC=C$\underline{H}$), 120.9 (NC=C$\underline{H}$), 144.2 (NC$\underline{=}$CH), 156.2 (OC$\underline{=}$CH), 167.0 (C=O), 167.1 (C=O); IR (KBr): $\tilde{\nu}$=1753, 1734 (C=O); HRMS (ESI): *m*/*z*: calcd for $C_{19}H_{27}NO_5Na^+$, 372.1781 $[M+Na]^+$; found 372.1797.

***O*-Ethyl-*O*-hexyl *trans*-1-(4-methoxyphenyl)aziridine-2,3-dicarboxylate (*trans*-2ac).** Yield: 12% (42 mg, 0.12 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz): δ=0.90 (t, ^3J(H,H)=7.0 Hz, 3H; C$\underline{H}_3$CH$_2$C), 1.24 (t, ^3J(H,H)=7.0 Hz, 3H; C$\underline{H}_3$CH$_2$O), 1.25–1.36 (m, 6H; CH$_3$(C$\underline{H}_2$)$_3$), 1.55–1.61 (m, 2H; C$\underline{H}_2$CH$_2$O), 3.43 (AB, ^3J(H,H)=2.4 Hz, 1H; HC$_{az}$), 3.44 (AB, ^3J(H,H)=2.4 Hz, 1H; HC$_{az}$), 3.76 (s, 3H; CH$_3$O), 4.03–4.14 (m, 2H; CH$_2$C$\underline{H}_2$O), 4.14–4.22 (m, 2H; CH$_3$C$\underline{H}_2$O), 6.78 (AA'BB', ^3J(H,H)=9.0 Hz, 2H; OC=CH), 6.85 (AA'BB', ^3J(H,H)=9.0 Hz, 2H; NC=CH); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=13.9 (C$\underline{H}_3$CH$_2$C), 14.0 (C$\underline{H}_3$CH$_2$O), 22.4 (CH$_3$C$\underline{H}_2$C), 25.4 (CH$_3$CH$_2$C$\underline{H}_2$), 28.3 (CH$_3$(CH$_2$)$_2$C$\underline{H}_2$), 31.3 (C$\underline{H}_2$CH$_2$O), 42.3 (C$_{az}$), 42.4 (C$_{az}$), 55.4 (CH$_3$O), 61.7 (CH$_3$C$\underline{H}_2$O), 65.9 (CH$_2$C$\underline{H}_2$O), 114.2 (OC=C$\underline{H}$), 120.7 (NC=C$\underline{H}$), 140.4 (NC$\underline{=}$CH), 155.9 (OC$\underline{=}$CH), 167.05 (C=O), 167.12 (C=O); IR (KBr): $\tilde{\nu}$=1738 (C=O); HRMS (ESI): *m*/*z*: calcd for $C_{19}H_{28}NO_5^+$, 350.1962 $[M+H]^+$; found 350.1969, calcd for $C_{19}H_{27}NO_5Na^+$, 372.1781 $[M+Na]^+$; found 372.1792.

***O*-Ethyl-*O*-octyl *cis*-1-(4-methoxyphenyl)aziridine-2,3-dicarboxylate (*cis*-2ad).** Yield: 73% (152 mg, 0.4 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz): δ=0.89 (t, ^3J(H,H)=6.8 Hz, 3H; C$\underline{H}_3$CH$_2$C), 1.33 (t, ^3J(H,H)=7.2 Hz, 3H; C$\underline{H}_3$CH$_2$O), 1.23–1.41 (m, 10H; CH$_3$(CH$_2$)$_5$), 1.66–1.74 (m, 2H; C$\underline{H}_2$CH$_2$O), 3.03 (s, 2H; HC$_{az}$), 3.77 (s, 3H; CH$_3$O), 4.21 (t, ^3J(H,H)=6.9 Hz, 2H; CH$_2$C$\underline{H}_2$O), 4.25–4.32 (m, 2H; CH$_3$C$\underline{H}_2$O), 6.81 (AA'BB', ^3J(H,H)=9.0 Hz, 2H; OC=CH), 6.97 (AA'BB', ^3J(H,H)=9.0 Hz, 2H; NC=CH); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=14.0 (C$\underline{H}_3$CH$_2$C), 14.1 (C$\underline{H}_3$CH$_2$O), 22.6 (CH$_3$C$\underline{H}_2$C), 25.8 (CH$_3$CH$_2$C$\underline{H}_2$), 28.5

($CH_3(CH_2)_2\underline{C}H_2$), 29.1 ($CH_3(CH_2)_3\underline{C}H_2$), 29.2 ($CH_3(CH_2)_4\underline{C}H_2$), 31.7 ($\underline{C}H_2CH_2O$), 43.2 ($C_{az}$), 43.3 ($C_{az}$), 55.5 ($CH_3O$), 61.8 ($CH_3\underline{C}H_2O$), 66.0 ($CH_2\underline{C}H_2O$), 114.4 (OC=$\underline{C}$H), 120.9 (NC=$\underline{C}$H), 144.3 (N$\underline{C}$=CH), 156.2 (O$\underline{C}$=CH), 167.06 (C=O), 167.10 (C=O); IR (KBr): $\tilde{\nu}$=1739 (C=O); HRMS (ESI): *m*/*z*: calcd for $C_{21}H_{31}NO_5Na^+$, 400.2094 $[M+Na]^+$; found 400.2114.

***O*-Ethyl-*O*-octyl *trans*-1-(4-methoxyphenyl)aziridine-2,3-dicarboxylate (*trans*-2ad).** Yield: 6% (12 mg, 0.03 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz): δ=0.90 (t, ^3J(H,H)=7.2 Hz, 3H; C$\underline{H}_3CH_2C$), 1.24 (t, ^3J(H,H)=7.0 Hz, 3H; C$\underline{H}_3CH_2O$), 1.25–1.35 (m, 10H; $CH_3(C\underline{H}_2)_5$), 1.55–1.61 (m, 2H; C$\underline{H}_2CH_2O$), 3.43 (AB, ^3J(H,H)=2.3 Hz, 1H; HC_{az}), 3.44 (AB, ^3J(H,H)=2.3 Hz, 1H; HC_{az}), 3.76 (s, 3H; CH_3O), 4.05–4.14 (m, 2H; $CH_2C\underline{H}_2O$), 4.14–4.23 (m, 2H; $CH_3C\underline{H}_2O$), 6.78 (AA'BB', ^3J(H,H)=9.0 Hz, 2H; OC=CH), 6.85 (AA'BB', ^3J(H,H)=9.0 Hz, 2H; NC=CH);^{13}C NMR ($CDCl_3$, 100 MHz): δ=14.04 ($\underline{C}H_3CH_2C$), 14.05 ($\underline{C}H_3CH_2O$), 22.6 ($CH_3\underline{C}H_2C$), 25.7 ($CH_3CH_2\underline{C}H_2$), 28.4 ($CH_3(CH_2)_2\underline{C}H_2$), 29.10 ($CH_3(CH_2)_3\underline{C}H_2$), 29.12 ($CH_3(CH_2)_4\underline{C}H_2$), 31.7 ($\underline{C}H_2CH_2O$), 42.3 ($C_{az}$), 42.4 ($C_{az}$), 55.4 ($CH_3O$), 61.8 ($CH_3\underline{C}H_2O$), 66.0 ($CH_2\underline{C}H_2O$), 114.2 (OC=$\underline{C}$H), 120.7 (NC=$\underline{C}$H), 140.4 (N$\underline{C}$=CH), 155.9 (O$\underline{C}$=CH), 167.08 (C=O), 167.12 (C=O); IR (KBr): $\tilde{\nu}$=1739 (C=O); HRMS (ESI): *m*/*z*: calcd for $C_{21}H_{32}NO_5^+$, 378.2275 $[M+H]^+$; found 378.2276, calcd for $C_{21}H_{31}NO_5Na^+$, 400.2094 $[M+Na]^+$; found 400.2101.

Dibutyl *cis*-1-(4-methoxyphenyl)aziridine-2,3-dicarboxylate (*cis*-2bb). Yield: 82% (144 mg, 0.41 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz): δ=0.96 (t, ^3J(H,H)=7.3 Hz, 6H; C$\underline{H}_3CH_2C$), 1.36–1.48 (m, 4H; $CH_3C\underline{H}_2C$), 1.64–1.74 (m, 4H; C$\underline{H}_2CH_2O$), 3.03 (s, 2H; HC_{az}), 3.78 (s, 3H; CH_3O), 4.23 (t, ^3J(H,H)=6.8 Hz, 4H; $CH_2C\underline{H}_2O$), 6.81 (AA'BB', ^3J(H,H)=9.0 Hz, 2H; OC=CH), 6.96 (AA'BB', ^3J(H,H)=9.0 Hz, 2H; NC=CH); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=13.6 ($\underline{C}H_3CH_2C$), 19.0 ($CH_3\underline{C}H_2C$), 30.5 ($\underline{C}H_2CH_2O$), 43.3 (C_{az}), 55.4 (CH_3O), 65.6 ($CH_2\underline{C}H_2O$), 114.4 (OC=$\underline{C}$H), 120.9 (NC=$\underline{C}$H), 144.3 (N$\underline{C}$=CH), 156.2 (O$\underline{C}$=CH), 167.1 (C=O); IR (KBr): $\tilde{\nu}$=1734, 1754 (C=O); HRMS (ESI): *m*/*z*: calcd for $C_{19}H_{28}NO_5^+$, 350.1962 $[M+H]^+$; found 350.1968.

Dibutyl *trans*-1-(4-methoxyphenyl)aziridine-2,3-dicarboxylate (*trans*-2bb). Yield: 17% (30 mg, 0.09 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz): δ=0.92 (t, ^3J(H,H)=7.3 Hz, 6H; C$\underline{H}_3CH_2C$), 1.29–1.36 (m, 4H; $CH_3C\underline{H}_2C$), 1.54–1.61 (m, 4H; C$\underline{H}_2CH_2O$), 3.43 (s, 2H; HC_{az}), 3.76 (s, 3H; CH_3O), 4.06–4.14 (m, 4H; $CH_2C\underline{H}_2O$), 6.78 (AA'BB', ^3J(H,H)=9.0 Hz, 2H; OC=CH), 6.84 (AA'BB', ^3J(H,H)=9.0 Hz, 2H; NC=CH); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=13.6 ($\underline{C}H_3CH_2C$), 19.0 ($CH_3\underline{C}H_2C$), 30.4 ($\underline{C}H_2CH_2O$), 42.3 (C_{az}), 55.4 (CH_3O), 65.6 ($CH_2\underline{C}H_2O$), 114.2 (OC=$\underline{C}$H), 120.6 (NC=$\underline{C}$H), 140.4 (N$\underline{C}$=CH), 155.9 (O$\underline{C}$=CH), 167.1

(C=O); IR (KBr): $\tilde{\nu}$=1737 (C=O); HRMS (ESI): *m*/*z*: calcd for $C_{19}H_{28}NO_5^+$, 350.1962 $[M+H]^+$; found 350.1971.

Dihexyl *cis*-1-(4-methoxyphenyl)aziridine-2,3-dicarboxylate (*cis*-2cc). Yield: 86 % (174 mg, 0.43 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz): δ=0.90 (t, ^3J(H,H)=7.2 Hz, 6H; C$\underline{H}_3$CH$_2$C), 1.25–1.41 (m, 12H; CH$_3$(C$\underline{H}_2$)$_3$), 1.65–1.73 (m, 4H; C$\underline{H}_2$CH$_2$O), 3.02 (s, 2H; HC$_{az}$), 3.76 (s, 3H; CH$_3$O), 4.20 (t, ^3J(H,H)=7.0 Hz, 4H; CH$_2$C$\underline{H}_2$O), 6.80 (AA'BB', ^3J(H,H)=9.0 Hz, 2H; OC=CH), 6.95 (AA'BB', ^3J(H,H)=9.0 Hz, 2H; NC=CH); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=13.9 (C$\underline{H}_3$CH$_2$C), 22.5 (CH$_3$C$\underline{H}_2$C), 25.4 (CH$_3$CH$_2$C$\underline{H}_2$C), 28.4 (CH$_3$(CH$_2$)$_2$C$\underline{H}_2$C), 31.4 (C$\underline{H}_2$CH$_2$O), 43.3 (C$_{az}$), 55.4 (CH$_3$O), 65.9 (CH$_2$C$\underline{H}_2$O), 114.4 (OC=C$\underline{H}$), 120.9 (NC=C$\underline{H}$), 144.3 (NC=CH), 156.2 (OC=CH), 167.1 (C=O); IR (KBr): $\tilde{\nu}$=1755, 1734 (C=O); HRMS (ESI): *m*/*z*: calcd for $C_{23}H_{36}NO_5^+$, 406.2588 $[M+H]^+$; found 406.2567, calcd for $C_{23}H_{35}NO_5Na^+$, 428.2407 $[M+Na]^+$; found 428.2418.

Dihexyl *trans*-1-(4-methoxyphenyl)aziridine-2,3-dicarboxylate (*trans*-2cc). Yield: 10% (21 mg, 0.05 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz): δ=0.90 (t, ^3J(H,H)=7.0 Hz, 6H; C$\underline{H}_3$CH$_2$C), 1.25–1.40 (m, 12H; CH$_3$(C$\underline{H}_2$)$_3$), 1.53–1.63 (m, 4H; C$\underline{H}_2$CH$_2$O), 3.43 (s, 2H; HC$_{az}$), 3.76 (s, 3H; CH$_3$O), 4.04-4.20 (m, 4H; CH$_2$C$\underline{H}_2$O), 6.78 (AA'BB', ^3J(H,H)=9.0 Hz, 2H; OC=CH), 6.84 (AA'BB', ^3J(H,H)=9.0 Hz, 2H; NC=CH); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=13.9 (C$\underline{H}_3$CH$_2$C), 22.5 (CH$_3$C$\underline{H}_2$C), 25.4 (CH$_3$CH$_2$C$\underline{H}_2$C), 28.4 (CH$_3$(CH$_2$)$_2$C$\underline{H}_2$C), 31.3 (C$\underline{H}_2$CH$_2$O), 42.4 (C$_{az}$), 55.3 (CH$_3$O), 65.9 (CH$_2$C$\underline{H}_2$O), 114.2 (OC=C$\underline{H}$), 120.6 (NC=C$\underline{H}$), 140.4 (NC=CH), 155.9 (OC=CH), 167.2 (C=O); IR (KBr): $\tilde{\nu}$=1739; HRMS (ESI): *m*/*z*: calcd for $C_{23}H_{35}NO_5Na^+$, 428.2407 $[M+Na]^+$; found 428.2429.

General procedure for the synthesis of pyrrolofullerenes 5. A solution of aziridine **2** (1 eq) and fullerene C_{60} (1.33 eq) in dry *o*-dichlorobenzene (2 ml) was stirred at 100 °C until consumption of the aziridine (control by TLC). Reaction mixture was separated by column chromatography (silica gel, toluene) to afford product as brown solid.

Pyrrolofullerene *trans*-5ab. Reaction time: 12 h. Yield: 49% (39 mg, 0.037 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz): δ=0.83 (t, ^3J(H,H)=7.4 Hz, 3H; C$\underline{H}_3$CH$_2$C), 1.17 (t, ^3J(H,H)=7.1 Hz, 3H; C$\underline{H}_3$CH$_2$O), 1.26–1.28 (m, 2H; CH$_3$C$\underline{H}_2$C), 1.53–1.55 (m, 2H; C$\underline{H}_2$CH$_2$O), 3.89 (s, 3H; CH$_3$O), 4.14–4.22 (m, 2H; CH$_2$C$\underline{H}_2$O), 4.22–4.30 (m, 2H; CH$_3$C$\underline{H}_2$O), 6.50 (s, 2H, $\underline{H}$C$_{Pyr}$), 7.02 (AA'BB', ^3J(H,H)=8.9 Hz, 2H; OC=C$\underline{H}$), 7.36 (AB, ^3J(H,H)=8.9 Hz, 2H; NC=C$\underline{H}$); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=13.6 (C$\underline{H}_3$CH$_2$C), 14.2 (C$\underline{H}_3$CH$_2$O), 19.0 (CH$_3$C$\underline{H}_2$C), 30.5 (C$\underline{H}_2$CH$_2$O), 55.5 (CH$_3$O), 61.7 (CH$_3$C$\underline{H}_2$O), 65.5 (CH$_2$C$\underline{H}_2$O),

71.2 ($C^{3/4}$), 71.23 ($C^{3/4}$), 74.6 ($C^{2/5}$), 74.9 ($C^{2/5}$), 114.8 (OC=CH), 121.0 (NC=CH), 136.32, 136.34, 136.97, 137.0 ($C_{fullerene}$), 138.5 (NC=CH), 139.6, 139.7, 140.2 (2C), 141.8 (2C), 141.81, 141.83, 141.9 (4C), 142.16 (2C), 142.22, 142.23, 142.7 (2C), 142.8 (2C), 143.1 (2C), 144.5 (2C), 144.6 (2C), 145.3 (2C), 145.4 (2C), 145.6, 145.61, 145.62 (2C), 145.73, 145.74 (2C), 145.75, 145.76, 145.8, 146.1 (4C), 146.38, 146.39, 146.42, 146.44, 147.5 (2C), 150.6, 150.7, 153.35, 153.40 ($C_{fullerene}$), 155.4 (OC=CH), 170.2 (C=O), 170.4 (C=O); IR (KBr): $\tilde{\nu}$=1724, 1751 (C=O); HRMS (ESI): *m*/*z*: calcd for $C_{77}H_{24}NO_5^+$, 1042.1649 $[M+H]^+$; found 1042.1692.

Pyrrolofullerene *cis*-5ab. Reaction time: 18 h. Yield: 48% (22 mg, 0.021 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz): δ=0.81 (t, ^3J(H,H)=7.3 Hz, 3H; CH_3CH_2C), 1.15 (t, ^3J(H,H)=7.2 Hz, 3H; CH_3CH_2O), 1.19–1.26 (m, 2H; CH_3CH_2C), 1.46–1.52 (m, 2H; CH_2CH_2O), 3.90 (s, 3H; CH_3O), 4.09–4.18 (m, 2H; CH_2CH_2O), 4.18–4.25 (m, 2H; CH_3CH_2O), 5.69 (s, 1H, HC_{Pyr}), 5.72 (s, 1H, HC_{Pyr}), 7.05 (AA'BB', ^3J(H,H)=9.0 Hz, 2H; OC=CH), 7.78 (AB, ^3J(H,H)=9.0 Hz, 2H; NC=CH); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=13.6 (CH_3CH_2C), 14.2 (CH_3CH_2O), 19.0 (CH_3CH_2C), 30.5 (CH_2CH_2O), 55.5 (CH_3O), 61.8 (CH_3CH_2O), 65.6 (CH_2CH_2O), 71.40 ($C^{3/4}$), 71.44 ($C^{3/4}$), 77.9 ($C^{2/5}$), 78.2 ($C^{2/5}$), 114.5 (OC=CH), 126.5 (NC=CH), 135.55, 135.59, 137.75 ($C_{fullerene}$), 137.76 (NC=CH), 137.79, 139.7, 139.8, 139.9 (2C), 141.8 (2C), 141.89, 141.91, 142.01 (3C), 142.03, 142.19, 142.20, 142.3 (2C), 143.73 (2C), 142.74 (2C), 143.1, 143.2, 144.41, 144.42, 144.67, 144.68, 145.32 (2C), 145.34 (2C), 145.4, 145.48, 145.49 (2C), 145.6, 145.76, 145.77 (2C), 146.10 (2C), 146.13 (2C), 146.25, 146.27, 146.34 (2C), 146.46, 146.47, 147.5 (2C), 150.9, 151.0, 152.4, 152.5 ($C_{fullerene}$), 158.0 (OC=CH), 168.3 (C=O), 168.4 (C=O); IR (KBr): $\tilde{\nu}$=1729, 1755 (C=O); HRMS (ESI): *m*/*z*: calcd for $C_{77}H_{24}NO_5^+$, 1042.1649 $[M+H]^+$; found 1042.1671.

Pyrrolofullerene *trans*-5ac. Reaction time: 19 h. Yield: 57% (41 mg, 0.038 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz): δ=0.85 (t, ^3J(H,H)=7.0 Hz, 3H; CH_3CH_2C), 1.17 (t, ^3J(H,H)=7.2 Hz, 3H; CH_3CH_2O), 1.17–1.27 (m, 6H; $CH_3(CH_2)_3C$), 1.50–1.59 (m, 2H; CH_2CH_2O), 3.87 (s, 3H; CH_3O), 4.12–4.21 (m, 2H; CH_2CH_2O), 4.21–4.30 (m, 2H; CH_3CH_2O), 6.50 (s, 1H, HC_{Pyr}), 6.51 (s, 1H, HC_{Pyr}), 7.02 (AA'BB', ^3J(H,H)=9.0 Hz, 2H; OC=CH), 7.35 (AB, ^3J(H,H)=9.0 Hz, 2H; NC=CH); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=14.0 (CH_3CH_2C), 14.2 (CH_3CH_2O), 22.5 (CH_3CH_2C), 25.6 ($CH_3CH_2CH_2$), 28.5 ($CH_3(CH_2)_2CH_2$), 31.3 (CH_2CH_2O), 55.5 (CH_3O), 61.7 (CH_3CH_2O), 65.9 (CH_2CH_2O), 71.21 ($C^{3/4}$), 71.24 ($C^{3/4}$), 74.6 ($C^{2/5}$), 74.9 ($C^{2/5}$), 114.8 (OC=CH), 120.9 (NC=CH), 136.32, 136.34, 136.97, 136.98, ($C_{fullerene}$), 138.5 (NC=CH), 139.6, 139.7, 140.15, 140.17, 141.79, 141.80, 141.81, 141.83, 141.9 (4C), 142.16, 142.17, 142.22 (2C),

142.7 (2C), 142.8 (2C), 143.1 (2C), 144.50, 144.51, 144.56, 144.57, 145.3 (2C), 145.4 (2C), 145.59, 145.62 (2C), 145.63, 145.73 (3C), 145.76, 145.78, 145.82, 146.1 (4C), 146.38 (2C), 146.43, 146.44, 147.49 (2C), 150.65, 150.68, 153.37, 153.41 ($C_{fullerene}$), 155.4 (O<u>C</u>=CH), 170.2 (C=O), 170.4 (C=O); IR (KBr): $\tilde{\nu}$=1730, 1755 (C=O); HRMS (ESI): *m*/*z*: calcd for $C_{79}H_{28}NO_5^+$, 1070.1962 $[M+H]^+$; found 1070.1984; calcd for $C_{79}H_{27}NO_5Na^+$, 1092.1781 $[M+Na]^+$; found 1092.1799.

Pyrrolofullerene *cis*-5ac.

Reaction time: 19 h. Yield: 59% (42 mg, 0.039 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz): δ=0.84 (t, ^3J(H,H)=7.2 Hz, 3H; C<u>H</u>$_3$CH$_2$C), 1.15 (t, ^3J(H,H)=7.2 Hz, 3H; C<u>H</u>$_3$CH$_2$O), 1.17–1.27 (m, 6H; CH-$_3$(C<u>H</u>$_2$)$_3$C), 1.47–1.54 (m, 2H; C<u>H</u>$_2$CH$_2$O), 3.90 (s, 3H; CH$_3$O), 4.10–4.18 (m, 2H; CH$_2$C<u>H</u>$_2$O), 4.18–4.26 (m, 2H; CH$_3$C<u>H</u>$_2$O), 5.70 (s, 1H, <u>H</u>C$_{Pyr}$), 5.72 (s, 1H, <u>H</u>C$_{Pyr}$), 7.05 (AA'BB', ^3J(H,H)=8.9 Hz, 2H; OC=C<u>H</u>), 7.78 (AB, ^3J(H,H)=8.9 Hz, 2H; NC=C<u>H</u>); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=14.0 (<u>C</u>H$_3$CH$_2$C), 14.2 (<u>C</u>H$_3$CH$_2$O), 22.5 (CH$_3$<u>C</u>H$_2$C), 25.5 (CH$_3$CH$_2$<u>C</u>H$_2$), 28.5 (CH$_3$(CH$_2$)$_2$<u>C</u>H$_2$), 31.3 (<u>C</u>H$_2$CH$_2$O), 55.5 (CH$_3$O), 61.7 (CH$_3$<u>C</u>H$_2$O), 66.0 (CH$_2$<u>C</u>H$_2$O), 71.38 (C$^{3/4}$), 71.43 (C$^{3/4}$), 77.9 (C$^{2/5}$), 78.1 (C$^{2/5}$), 114.5 (OC=<u>C</u>H), 126.4 (NC=<u>C</u>H), 135.5, 135.6, 137.73 ($C_{fullerene}$), 137.75 (N<u>C</u>=CH), 137.78, 139.66, 139.72, 139.89, 139.90, 141.7 (2C), 141.88, 141.89, 141.99 (3C), 142.01, 142.17, 142.19, 142.23, 142.24, 142.70 (2C), 142.72 (2C), 143.0, 143.2, 144.39, 144.41, 144.7 (2C), 145.30 (2C), 145.32 (2C), 145.43, 145.47 (2C), 145.49, 145.6, 145.73, 145.75 (2C), 146.09 (2C), 146.11 (2C), 146.23, 146.24, 146.32 (2C), 146.45 (2C), 147.4 (2C), 150.8, 151.0, 152.43, 152.45 ($C_{fullerene}$), 158.0 (O<u>C</u>=CH), 168.3 (C=O), 168.4 (C=O); IR (KBr): $\tilde{\nu}$=1729, 1746 (C=O); HRMS (ESI): *m*/*z*: calcd for $C_{79}H_{28}NO_5^+$, 1070.1962 $[M+H]^+$; found 1070.1915; calcd for $C_{79}H_{27}NO_5Na^+$, 1092.1781 $[M+Na]^+$; found 1092.1819.

Pyrrolofullerene *trans*-5ad. Reaction time: 18 h. Yield: 38% (26 mg, 0.024 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz): δ=0.86 (t, ^3J(H,H)=6.9 Hz, 3H; C<u>H</u>$_3$CH$_2$C), 1.17 (t, ^3J(H,H)=7.2 Hz, 3H; C<u>H</u>$_3$CH$_2$O), 1.11–1.33 (m, 10H; CH$_3$(C<u>H</u>$_2$)$_5$), 1.50–1.60 (m, 2H; C<u>H</u>$_2$CH$_2$O), 3.87 (s, 3H; CH$_3$O), 4.13–4.21 (m, 2H; CH$_2$C<u>H</u>$_2$O), 4.21–4.30 (m, 2H; CH$_3$C<u>H</u>$_2$O), 6.50 (s, 1H, <u>H</u>C$_{Pyr}$), 6.51 (s, 1H, <u>H</u>C$_{Pyr}$), 7.02 (AA'BB', ^3J(H,H)=8.9 Hz, 2H; OC=C<u>H</u>), 7.35 (AB, ^3J(H,H)=8.9 Hz, 2H; NC=C<u>H</u>); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=14.1 (<u>C</u>H$_3$CH$_2$C), 14.2 (<u>C</u>H$_3$CH$_2$O), 22.6 (CH$_3$<u>C</u>H$_2$C), 25.9 (CH$_3$CH$_2$<u>C</u>H$_2$), 28.6 (CH$_3$(CH$_2$)$_2$<u>C</u>H$_2$), 29.13 (CH$_3$(CH$_2$)$_3$<u>C</u>H$_2$), 29.14 (CH$_3$(CH$_2$)$_4$<u>C</u>H$_2$), 31.8 (<u>C</u>H$_2$CH$_2$O), 55.5 (CH$_3$O), 61.7 (CH$_3$<u>C</u>H$_2$O), 66.0 (CH$_2$<u>C</u>H$_2$O), 71.22 (C$^{3/4}$), 71.24 (C$^{3/4}$), 74.6 (C$^{2/5}$), 74.9 (C$^{2/5}$), 114.8 (OC=<u>C</u>H), 120.9 (NC=<u>C</u>H), 136.3, 136.4, 136.97, 137.0 (2C) ($C_{fullerene}$), 138.5 (N<u>C</u>=CH), 139.66, 139.71, 140.16, 140.17, 141.80, 141.81,

141.82, 141.84, 141.9 (4C), 142.17 (2C), 142.23, 142.24, 142.7 (2C), 142.8 (2C), 143.12, 143.13, 144.51, 144.52, 144.57, 144.58, 145.3 (2C), 145.4 (2C), 145.61, 145.63 (2C), 145.64, 145.7 (3C), 145.77, 145.79, 145.82, 146.1 (4C), 146.40 (2C), 146.44, 146.5, 147.5, 150.65, 150.70, 153.37, 154.41 ($C_{fullerene}$), 155.4 (O<u>C</u>=CH), 170.2 (C=O), 170.4 (C=O); IR (KBr): $\tilde{\nu}$=1731, 1754 (C=O); HRMS (ESI): *m*/*z*: calcd for $C_{81}H_{32}NO_5^+$, 1098.2275 $[M+H]^+$; found 1098.2297.

Pyrrolofullerene *cis*-5ad. Reaction time: 19 h. Yield: 42% (20 mg, 0.018 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz): δ=0.86 (t, ^3J(H,H)=7.2 Hz, 3H; C<u>H</u>$_3$CH$_2$C), 1.15 (t, ^3J(H,H)=7.2 Hz, 3H; C<u>H</u>$_3$CH$_2$O), 1.16–1.35 (m, 10H; CH$_3$(C<u>H</u>$_2$)$_5$), 1.47–1.55 (m, 2H; C<u>H</u>$_2$CH$_2$O), 3.90 (s, 3H; CH$_3$O), 4.10–4.18 (m, 2H; CH$_2$C<u>H</u>$_2$O), 4.19–4.25 (m, 2H; CH$_3$C<u>H</u>$_2$O), 5.70 (s, 1H, <u>H</u>C$_{Pyr}$), 5.72 (s, 1H, <u>H</u>C$_{Pyr}$), 7.05 (AA'BB', ^3J(H,H)=9.0 Hz, 2H; OC=C<u>H</u>), 7.77 (AB, ^3J(H,H)=9.0 Hz, 2H; NC=C<u>H</u>); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=14.1 (<u>C</u>H$_3$CH$_2$C), 14.2 (<u>C</u>H$_3$CH$_2$O), 22.6 (CH$_3$<u>C</u>H$_2$C), 25.9 (CH$_3$CH$_2$<u>C</u>H$_2$), 28.6 (CH$_3$(CH$_2$)$_2$<u>C</u>H$_2$), 29.14 (2C, CH$_3$(CH$_2$)$_3$<u>C</u>H$_2$, CH$_3$(CH$_2$)$_4$<u>C</u>H$_2$), 31.8 (<u>C</u>H$_2$CH$_2$O), 55.5 (CH$_3$O), 61.8 (CH$_3$<u>C</u>H$_2$O), 66.0 (CH$_2$<u>C</u>H$_2$O), 71.40 (C$^{3/4}$), 71.44 (C$^{3/4}$), 77.9 (C$^{2/5}$), 78.1 (C$^{2/5}$), 114.5 (OC=<u>C</u>H), 126.5 (NC=<u>C</u>H), 135.55, 135.58, 137.75 ($C_{fullerene}$), 137.76 (N<u>C</u>=CH), 137.80, 139.68, 139.74, 139.90, 139.91, 141.8 (2C), 141.89, 141.91, 142.00 (3C), 142.03, 142.19 (2C), 142.25 (2C), 142.72, 142.73, 142.74 (2C), 143.1, 143.2, 144.41, 144.42, 144.7 (2C), 145.31 (2C), 145.34 (2C), 145.45, 145.48 (2C), 145.50, 145.6, 145.74, 145.76 (2C), 146.10 (2C), 146.13 (2C), 146.25, 146.26, 146.34 (2C), 146.5 (2C), 147.5 (2C), 150.85, 150.97, 152.43, 152.46 ($C_{fullerene}$), 158.0 (O<u>C</u>=CH), 168.3 (C=O), 168.4 (C=O); IR (KBr): $\tilde{\nu}$=1728, 1755 (C=O); HRMS (ESI): *m*/*z*: calcd for $C_{81}H_{31}NO_5Na^+$, 1120.2094 $[M+Na]^+$; found 1120.2073.

Pyrrolofullerene *trans*-5bb.

Reaction time: 16 h. Yield: 57% (41 mg, 0.038 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz): δ=0.83 (t, ^3J(H,H)=7.3 Hz, 6H; C<u>H</u>$_3$CH$_2$C), 1.20–1.30 (m, 4H; CH$_3$C<u>H</u>$_2$C), 1.49–1.56 (m, 4H; C<u>H</u>$_2$CH$_2$O), 3.88 (s, 3H; CH$_3$O), 4.14–4.25 (m, 4H; CH$_2$C<u>H</u>$_2$O), 6.51 (s, 2H, <u>H</u>C$_{Pyr}$), 7.02 (AA'BB', ^3J(H,H)=8.9 Hz, 2H; OC=C<u>H</u>), 7.35 (AB, ^3J(H,H)=8.9 Hz, 2H; NC=C<u>H</u>); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=13.6 (<u>C</u>H$_3$CH$_2$C), 19.0 (CH$_3$<u>C</u>H$_2$C), 30.5 (<u>C</u>H$_2$CH$_2$O), 55.5 (CH$_3$O), 65.5 (CH$_2$<u>C</u>H$_2$O), 71.3 (2C, C$^{3/4}$), 74.8 (2C, C$^{2/5}$), 114.8 (OC=<u>C</u>H), 121.0 (NC=<u>C</u>H), 136.4 (2C), 137.0 (2C) ($C_{fullerene}$), 138.5 (N<u>C</u>=CH), 139.7 (2C), 140.1 (2C), 141.8 (2C), 141.84 (2C), 141.94 (4C), 142.16 (2C), 142.23 (2C), 142.68 (2C), 142.75 (2C), 143.1 (2C), 144.5 (2C), 144.6 (2C), 145.3 (2C), 145.4 (2C), 145.6 (2C), 145.63 (2C), 145.7 (4C), 145.8 (2C), 146.1 (4C), 146.39 (2C), 146.42 (2C), 147.5 (2C), 150.7 (2C), 153.40 (2C) ($C_{fullerene}$), 155.4 (O<u>C</u>=CH), 170.3

(C=O); IR (KBr): $\tilde{\nu}$=1728, 1753 (C=O); HRMS (ESI): *m*/*z*: calcd for $C_{79}H_{28}NO_5^+$, 1070.1962 $[M+H]^+$; found 1070.2000.

Pyrrolofullerene *cis*-5bb. Reaction time: 5 h. Yield: 25% (18 mg, 0.017 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz): δ=0.81 (t, ^3J(H,H)=7.2 Hz, 6H; $C\underline{H}_3CH_2C$), 1.19–1.29 (m, 4H; $CH_3C\underline{H}_2C$), 1.46–1.53 (m, 4H; $C\underline{H}_2CH_2O$), 3.90 (s, 3H; CH_3O), 4.08–4.21 (m, 4H; $CH_2C\underline{H}_2O$), 5.71 (s, 2H, $\underline{H}C_{Pyr}$), 7.05 (AA'BB', ^3J(H,H)=8.9 Hz, 2H; OC=C$\underline{H}$), 7.77 (AB, ^3J(H,H)=8.9 Hz, 2H; NC=C$\underline{H}$); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=13.6 ($\underline{C}H_3CH_2C$), 19.0 ($CH_3\underline{C}H_2C$), 30.5 ($\underline{C}H_2CH_2O$), 55.5 (CH_3O), 65.6 ($CH_2\underline{C}H_2O$), 71.40 (2C, $C^{3/4}$), 78.2 (2C, $C^{2/5}$), 114.5 (OC=$\underline{C}$H), 126.5 (NC=$\underline{C}$H), 135.6 (2C; $C_{fullerene}$), 137.8 (3C; 2$C_{fullerene}$ + N$\underline{C}$=CH), 139.7 (2C), 139.9 (2C), 141.8 (2C), 141.9 (2C), 142.01 (2C), 142.03 (2C), 142.2 (2C), 142.3 (2C), 142.72 (2C), 142.73 (2C), 143.1, 143.2, 144.4 (2C), 144.7 (2C), 145.31 (2C), 145.33 (2C), 145.4 (2C), 145.5 (2C), 145.6, 145.76 (2C), 145.78, 146.10 (2C), 146.13 (2C), 146.27 (2C), 146.34 (2C), 146.5 (2C), 147.5 (2C), 151.0 (2C), 152.4 (2C) ($C_{fullerene}$), 158.1 (O$\underline{C}$=CH), 168.4 (C=O); IR (KBr): $\tilde{\nu}$=1727, 1753 (C=O); HRMS (ESI): *m*/*z*: calcd for $C_{79}H_{28}NO_5^+$, 1070.1962 $[M+H]^+$; found 1070.1941.

Pyrrolofullerene *trans*-5cc.

Reaction time: 19 h. Yield: 50% (38 mg, 0.034 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz): δ=0.86 (t, ^3J(H,H)=7.0 Hz, 6H; $C\underline{H}_3CH_2C$), 1.16–1.29 (m, 12H; $CH_3(C\underline{H}_2)_3C$), 1.50–1.58 (m, 4H; $C\underline{H}_2CH_2O$), 3.87 (s, 3H; CH_3O), 4.10–4.22 (m, 4H; $CH_2C\underline{H}_2O$), 6.51 (s, 2H, $\underline{H}C_{Pyr}$), 7.02 (AA'BB', ^3J(H,H)=9.0 Hz, 2H; OC=C$\underline{H}$), 7.35 (AA'BB', ^3J(H,H)=9.0 Hz, 2H; NC=C$\underline{H}$); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=14.0 ($\underline{C}H_3CH_2C$), 22.5 ($CH_3\underline{C}H_2C$), 25.6 ($CH_3CH_2\underline{C}H_2$), 28.5 ($CH_3(CH_2)_2\underline{C}H_2$), 31.3 ($\underline{C}H_2CH_2O$), 55.4 ($CH_3O$), 65.9 ($CH_2\underline{C}H_2O$), 71.2 (2C, $C^{3/4}$), 74.8 (2C, $C^{2/5}$), 114.8 (OC=$\underline{C}$H), 121.0 (NC=$\underline{C}$H), 136.3 (2C), 137.0 (2C) ($C_{fullerene}$), 138.5 (N$\underline{C}$=CH), 139.7 (2C), 140.1 (2C), 141.78 (2C), 141.83 (2C), 141.92 (2C), 141.93 (2C), 142.16 (2C), 142.22 (2C), 142.67 (2C), 142.75 (2C), 143.1 (2C), 144.5 (2C), 144.6 (2C), 145.29 (2C), 145.35 (2C), 145.59 (2C), 145.62 (2C), 145.7 (4C), 145.8 (2C), 146.1 (4C), 146.38 (2C), 146.42 (2C), 147.5 (2C), 150.7 (2C), 153.40 (2C) ($C_{fullerene}$), 155.4 (O$\underline{C}$=CH), 170.3 (C=O); IR (KBr): $\tilde{\nu}$=1728, 1752 (C=O); HRMS (ESI): *m*/*z*: calcd for $C_{83}H_{35}NO_5Na$, 1148.2407 $[M+Na]^+$; found 1148.2396.

Pyrrolofullerene *cis*-5cc.

Reaction time: 19 h. Yield: 58% (32 mg, 0.028 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz): δ=0.84 (t, ^3J(H,H)=7.0 Hz, 6H; $C\underline{H}_3CH_2C$), 1.15–1.25 (m, 12H; $CH_3(C\underline{H}_2)_3C$), 1.46–1.55 (m, 4H; $C\underline{H}_2CH_2O$), 3.89 (s, 3H; CH_3O), 4.08–4.20 (m, 4H; $CH_2C\underline{H}_2O$), 5.71 (s, 2H, $\underline{H}C_{Pyr}$), 7.04 (AA'BB', ^3J(H,H)=8.9 Hz, 2H;

OC=CH), 7.77 (AA'BB', ^3J(H,H)=8.9 Hz, 2H; NC=CH); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=14.0 (CH_3CH_2C), 22.5 (CH_3CH_2C), 25.6 ($CH_3CH_2CH_2C$), 28.5 ($CH_3(CH_2)_2CH_2C$), 31.3 (CH_2CH_2O), 55.4 (CH_3O), 66.0 (CH_2CH_2O), 71.4 (2C, $C^{3/4}$), 78.1 (2C, $C^{2/5}$), 114.5 (OC=CH), 126.5 (NC=CH), 135.6 (2C; $C_{fullerene}$), 137.8 (3C; $2C_{fullerene}$ + NC=CH), 139.7 (2C), 139.9 (2C), 141.7 (2C), 141.9 (2C), 142.00 (2C), 142.03 (2C), 142.20 (2C), 142.25 (2C), 142.71 (2C), 142.73 (2C), 143.1, 143.2, 144.4 (2C), 144.7 (2C), 145.31 (2C), 145.33 (2C), 145.4 (2C), 145.5 (2C), 145.6, 145.7 (3C), 146.10 (2C), 146.12 (2C), 146.27 (2C), 146.34 (2C), 146.5 (2C), 147.5 (2C), 151.0 (2C), 152.4 (2C) ($C_{fullerene}$), 158.0 (OC=CH), 168.4 (C=O); IR (KBr): $\tilde{\nu}$=1729, 1757 (C=O); HRMS (ESI): *m*/*z*: calcd for $C_{83}H_{36}NO_5^+$, 1126.2588 $[M+H]^+$; found 1126.2567; calcd for $C_{83}H_{35}NO_5Na^+$, 1148.2407 $[M+Na]^+$; found 1148.2398.

General procedure for the synthesis of nitro-porphyrins 6b-e. Iodine (25 mg, 0.1 mmol) was added to a solution of aldehyde **7** (0.75 mmol), *p*-nitrophenyldipyrromethane **(8)** (67 mg, 0.25 mmol) and pyrrole (34 mg, 0.5 mmol) in DCM (100 ml) at 35 °C and the mixture was stirred for 1¼–3 h (depending on the substrate, denoted as "condensation time" below). The solution was cooled to room temperature with cold water bath, chloranil (185 mg, 0.75 mmol) was immediately added and stirring was continued for another 15 min. The reaction mixture was quenched with 10% aq NaOH, washed with water and brine and dried over Na_2SO_4. The desiccant was filtered off, the solvent was removed *in vacuo* and the residue was separated by column chromatography (silica gel, DCM-hexane, 1:1) to afford products as violet crystals.

5,10,15-tris(4-bromophenyl)-20-(4-nitrophenyl)porphyrin (6b). Condensation time: 2.5 h. Yield: 13% (28.6 mg, 0.032 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz): δ=-2.84 (s, 2H; NH), 7.92 (AA'BB', ^3J(H,H)=8.3 Hz, 6H; HC_{Ar}), 8.08 (AA'BB', ^3J(H,H)=8.3 Hz, 6H; HC_{Ar}), 8.39 (AA'BB', ^3J(H,H)=8.7 Hz, 2H; HC_{ArNO2}), 8.65 (AA'BB', ^3J(H,H)=8.7 Hz, 2H; HC_{ArNO2}), 8.77 (AB, ^3J(H,H)=4.7 Hz, 2H; HC^{β}), 8.87 (s, 4H; HC^{β}), 8.88 (AB, ^3J(H,H)=4.7 Hz, 2H; HC^{β}); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=117.2, 119.3, 119.6, 121.9, 122.8, 126.4, 128.6, 129.7, 130.1, 131.2, 131.6 (br s), 135.1, 135.8, 140.66, 140.68, 147.8, 148.8; IR (KBr): $\tilde{\nu}$=3316 (N-H), 1518, 1339 cm^{-1} (NO_2); HRMS (ESI): *m*/*z*: calcd for $C_{44}H_{27}Br_3N_5O_2^+$, 893.9709 $[M+H]^+$; found: 893.9710.

5,10,15-tris(4-(trifluoromethyl)phenyl)-20-(4-nitrophenyl)porphyrin (6c). Condensation time: 3 h. Yield: 9% (20 mg, 0.023 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz): δ=-2.81 (s, 2H; NH), 8.07 (AA'BB', ^3J(H,H)=8.1 Hz, 6H; HC_{Ar}), 8.35 (AA'BB', ^3J(H,H)=8.1 Hz, 6H; HC_{Ar}), 8.41 (AA'BB', ^3J(H,H)=8.7 Hz,

2H; HC_{ArNO2}), 8.67 (AA'BB', ^{3}J(H,H)=8.7 Hz, 2H; HC_{ArNO2}), 8.80 (AB, ^{3}J(H,H)=4.8 Hz, 2H; HC^{β}), 8.83 (s, 4H; HC^{β}), 8.85 (AB, ^{3}J(H,H)=4.8 Hz, 2H; HC^{β}); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=117.7, 119.2, 119.3, 122.0, 123.9 (q, ^{4}J(C,F)=3.7 Hz), 124.0 (q, ^{1}J(C,F)=272.1 Hz), 130.4 (q, ^{3}J(C,F)=32.6 Hz), 131.5 (br s), 134.6, 135.1, 145.4 (q, ^{2}J(C,F)=1.3 Hz), 147.9, 148.6 (C_{Ar}); IR (KBr): $\tilde{\nu}$=3316 (N-H), 1520, 1324 cm^{-1} (NO_2); HRMS (ESI): *m*/*z*: calcd for $C_{47}H_{27}F_9N_5O_2^+$, 864.2016 $[M+H]^+$; found 864.1997**.**

5,10,15-tris(4-methylphenyl)-20-(4-nitrophenyl)porphyrin (6d). Condensation time: 1.5 h. Yield: 18% (31.4 mg, 0.045 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz): δ=-2.72 (s, 2H; NH), 2.73 (s, 9H; CH_3), 7.57-7.58 (m, 6H; HC_{Ar}), 8.10-8.12 (m, 6H; HC_{Ar}), 8.39 (AA'BB', ^{3}J(H,H)=8.7 Hz, 2H; HC_{ArNO2}), 8.62 (AA'BB', ^{3}J(H,H)=8.7 Hz, 2H; HC_{ArNO2}), 8.73 (AB, ^{3}J(H,H)=4.8 Hz, 2H; HC^{β}), 8.90 (s, 4H; HC^{β}) 8.93 (AB, ^{3}J(H,H)=4.8 Hz, 2H; HC^{β}); HRMS (ESI): *m*/*z*: calcd for $C_{47}H_{36}N_5O_2^+$, 702.2864 $[M+H]^+$; found 702.2859. ^{1}H NMR spectrum matches literature data. [34]

5,10,15-tris(4-methoxyphenyl)-20-(4-nitrophenyl)porphyrin (6e). Condensation time: 1¼ h. Compound was used in the following step without chromatographic separation from porphyrin by-products.

5,10,15-tris(2,4,6-trimethoxyphenyl)-20-(4-nitrophenyl)porphyrin (6f). Iodine (25 mg, 0.1 mmol) was added to a solution of 2,4,6-trimethoxybenzaldehyde **7f** (147 mg, 0.75 mmol), *p*-nitrophenyldipyrromethane **8** (67 mg, 0.25 mmol) and pyrrole (34 mg, 0.5 mmol) in $CHCl_3$ (100 ml) at 61 °C and the mixture was mechanically stirred for 1 h. The solution was cooled to 0 °C with ice bath, chloranil (185 mg, 0.75 mmol) was immediately added and stirring was continued for another 15 min. The reaction mixture was quenched with 10% aq NaOH, washed with water and brine and dried over Na_2SO_4. The desiccant was filtered off, the solvent was removed *in vacuo* and the residue was separated by column chromatography (silica gel, $CHCl_3$) to afford porphyrin **6f** as violet crystals. Yield: 12% (28.1 mg, 0.031 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz): δ=-2.56 (s, 2H; NH), 3.50 (s, 12H; CH_3), 3.52 (s, 6H; CH_3), 4.09 (s, 9H; CH_3), 6.58 (s, 6H; HC_{Ar}), 8.40 (AA'BB', ^{3}J(H,H)=8.7 Hz, 2H; HC_{ArNO2}), 8.60 (AA'BB', ^{3}J(H,H)=8.7 Hz, 2H; HC_{ArNO2}), 8.64 (AB, ^{3}J(H,H)=4.7 Hz, 2H; HC^{β}), 8.77 (s, 4H; HC^{β}) 8.82 (AB, ^{3}J(H,H)=4.7 Hz, 2H; HC^{β}); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=55.6, 56.02, 56.03 (CH_3), 90.8, 90.9, 111.6, 111.9, 112.7, 112.9, 115.2, 121.6, 129.5 (br s), 130.6 (br s), 135.1, 147.4, 150.1, 161.11, 161.13, 161.78,

161.82 ($\underline{C}_{Ar}$); IR (KBr): $\tilde{\nu}$=3320 (N-H), 1520, 1335 cm^{-1} (NO_2); HRMS (ESI): *m*/*z*: calcd for $C_{53}H_{48}N_5O_{11}^+$, 930.3345 $[M+H]^+$; found 930.3372.

General procedure for the synthesis of amino-porphyrins 12b-f. The mixture of nitro-porphyrin **6** and tin (II) chloride dihydrate in concentrated hydrochloric acid (5 ml) was stirred under argon at 70 °C for 1 to 5 h, depending on the substrate. The reaction mixture was poured on ice, neutralized with aqueous ammonia to pH 8, extracted with chloroform, washed with water and dried over Na_2SO_4. The desiccant was filtered off, the solvent was removed *in vacuo* and the residue was separated by column chromatography (silica gel, DCM) to afford products as violet crystals.

5-(4-aminophenyl)-10,15,20-tris(4-bromophenyl)porphyrin (12b). Reaction time: 5 h. Yield: 41% (15 mg, 0.017 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz): δ=-2.78 (s, 2H; N$\underline{H}$), 4.02 (br s, 2H; N$\underline{H}_2$), 7.05 (AA'BB', ^3J(H,H)=8.4 Hz, 2H; $\underline{H}C_{ArNH2}$), 7.89 (AA'BB', ^3J(H,H)=8.2 Hz, 6H; $\underline{H}C_{Ar}$), 7.98 (AA'BB', ^3J(H,H)=8.4 Hz, 2H; $\underline{H}C_{ArNH2}$), 8.07 (AA'BB', ^3J(H,H)=8.2 Hz, 6H; $\underline{H}C_{Ar}$), 8.82-8.84 (m, 6H; $\underline{H}C^{\beta}$), 8.98 (AB, ^3J(H,H)=4.7 Hz, 2H; $\underline{H}C^{\beta}$); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=113.5, 118.3, 118.6, 121.6, 122.49, 122.50, 129.90, 129.93, 130.9 (br s), 131.2, 132.0, 135.7, 135.8, 140.97, 141.05, 146.2 ($\underline{C}_{Ar}$); IR (KBr): $\tilde{\nu}$=3318 (NH), 3374, 3436 cm^{-1} (NH_2); HRMS (ESI): *m*/*z*: calcd for $C_{44}H_{29}Br_3N_5^+$, 863.9968 $[M+H]^+$; found 863.9953. NMR spectra match literature data. [35]

5-(4-aminophenyl)-10,15,20-tris(4-(trifluoromethyl)phenyl)porphyrin (12c). Reaction time: 5 h. Yield: 6% (14 mg, 0.016 mmol) for two steps from **7c**. In a separate experiment, the reduction was performed at 90 °C under argon atmosphere for 26h and the reaction mixture was treated as in general technique, which gave porphyrin **12c** in 26% yield (based on **6c**) along with porphyrin **13**.

Porphyrin **12c**. ^{1}H NMR ($CDCl_3$, 400 MHz): δ=-2.76 (s, 2H; N$\underline{H}$), 4.05 (br s, 2H; N$\underline{H}_2$), 7.08 (AA'BB', ^3J(H,H)=8.4 Hz, 2H; $\underline{H}C_{ArNH2}$), 8.00 (AA'BB', ^3J(H,H)=8.4 Hz, 2H; $\underline{H}C_{ArNH2}$), 8.04 (AA'BB', ^3J(H,H)=8.0 Hz, 6H; $\underline{H}C_{Ar}$), 8.34 (AA'BB', ^3J(H,H)=8.0 Hz, 6H; $\underline{H}C_{Ar}$), 8.78 (AB, ^3J(H,H)=4.7 Hz, 2H; $\underline{H}C^{\beta}$), 8.80 (s, 4H, $\underline{H}C^{\beta}$), 9.00 (AB, ^3J(H,H)=4.7 Hz, 2H; $\underline{H}C^{\beta}$); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=113.5, 118.0, 118.5, 122.1, 123.72 (q, ^4J(C,F)=3.7 Hz), 123.74 (q, ^4J(C,F)=3.7 Hz), 124.5 (q, ^1J(C,F)=272 Hz), 130.2 (q, ^3J(C,F)=32.5 Hz), 130.9 (br s), 131.8, 134.6, 135.8, 145.7 (q, ^2J(C,F)=1.4 Hz), 145.8 (q, ^2J(C,F)=1.4 Hz), 146.3 ($\underline{C}_{Ar}$); IR (KBr): $\tilde{\nu}$=3329 (NH), 3360, 3454 cm^{-1} (NH_2); HRMS (ESI): *m*/*z*: calcd for $C_{47}H_{29}F_9N_5^+$, 834.2274 $[M+H]^+$; found 834.2274.

Porphyrin **13**.5-(4-amino-3-chlorophenyl)-10,15,20-tris(4-(trifluoromethyl)phenyl)porphyrin (**13**)

NMR ^{1}H ($CDCl_3$, 400 MHz), δ: -2.80 s (2H, NH), 4.47 s (2H, NH_2), 7.17 d (1H, *J* 8.1 Hz, HC_{ArNH2}), 7.92 dd (1H, J_1 8.1 Hz, J_2 2.0 Hz, HC_{ArNH2}), 8.05 d (AA'BB') (6H, *J* 7.8 Hz, HC_{Ar}), 8.12 d (1H, *J* 2.0 Hz, HC_{ArNH2}), 8.35 d (AA'BB') (6H, *J* 7.8 Hz, HC_{Ar}), 8.79–8.83 m (6H, HC^{β}), 8.98 d (AB) (2H, *J* 4.8 Гц, HC^{β}); NMR ^{13}C ($CDCl_3$, 100 МГц), δ: 114.1, 118.1, 118.4, 118.7, 120.1, 123.8, 124.5 (q, *J* 272 Hz), 130.3 (q, *J* 32.5 Hz), 130.9 br s, 132.5, 134.0, 134.6, 135.2, 142.9, 145.7;

HRMS (ESI): *m*/*z*: calcd for $C_{47}H_{28}F_9ClN_5^+$, 868.1884 $[M+nH]^+$; found 868.1898.**5-(4-aminophenyl)-10,15,20-tris(4-methylphenyl)porphyrin (12d).** Reaction time: 5 h. Yield: 84% (26.4 mg, 0.039 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz): *δ*=-2.71 (s, 2H; NH), 2.72 (s, 9H; CH_3), 3.99 (br s, 2H; NH_2), 7.05 (AA'BB', ^{3}J(H,H)=8.4 Hz, 2H; HC_{ArNH2}), 7.57 (AA'BB', ^{3}J(H,H)=7.8 Hz, 6H; HC_{Ar}), 8.01 (AA'BB', ^{3}J(H,H)=8.4 Hz, 2H; HC_{ArNH2}), 8.12 (AA'BB', ^{3}J(H,H)=7.8 Hz, 6H; HC_{Ar}), 8.87-8.89 (m, 6H; HC^{β}), 8.94 (AB, ^{3}J(H,H)=4.7 Hz, 2H; HC^{β}); IR (KBr): $\tilde{\nu}$=3318 (NH), 3370, 3456 cm^{-1} (NH_2); HRMS (ESI): *m*/*z*: calcd for $C_{47}H_{38}N_5^+$, 672.3122 $[M+H]^+$; found 672.3125. ^{1}H NMR spectrum matches literature data. [36]

5-(4-aminophenyl)-10,15,20-tris(4-methoxyphenyl)porphyrin (12e). Reaction time: 5 h. Yield: 9% (33.7 mg, 0.047 mmol) for two steps (from **9e**). ^{1}H NMR ($CDCl_3$, 400 MHz): *δ*=-2.71 (s, 2H; NH), 4.02 (br s, 2H; NH_2), 4.11 (s, 9H; CH_3), 7.07 (AA'BB', ^{3}J(H,H)=8.4 Hz, 2H; HC_{ArNH2}), 7.29 (AA'BB', ^{3}J(H,H)=8.7 Hz, 6H; HC_{Ar}), 8.00 (AA'BB', ^{3}J(H,H)=8.4 Hz, 2H, $HC_{ArNH2)}$), 8.14 (AA'BB', ^{3}J(H,H)=8.7 Hz, 6H; HC_{Ar}), 8.86-8.88 (m, 6H; HC^{β}), 8.94 (AB, ^{3}J(H,H)=4.7 Hz, 2H; HC^{β}); ^{13}C NMR ($CDCl_3$, 100 MHz): *δ*=55.6 (CH_3), 112.2, 113.4, 119.5, 119.6, 120.6, 130.9, 132.5, 134.7, 134.8, 135.6, 135.7, 146.0, 159.4 (C_{Ar}); IR (KBr): $\tilde{\nu}$=3318 (NH), 3378, 3460 cm^{-1} (NH_2); HRMS (ESI): *m*/*z*: calcd for $C_{47}H_{38}N_5O_3^+$, 720.2969 $[M+H]^+$; found 720.2976. ^{1}H NMR spectrum matches literature data.[37]

5-(4-aminophenyl)-10,15,20-tris(2,4,6-trimethoxyphenyl)porphyrin (12f). Reaction time: 1 h. Yield: 55% (8 mg, 0.009 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz): *δ*=-2.56 (s, 2H; NH), 3.48 (s, 12H; CH_3), 3.50 (s, 6H; CH_3), 3.98 (br s, 2H; NH_2), 4.09 (s, 9H; CH_3), 6.57 (s, 6H; HC_{Ar}), 7.02 (AA'BB', ^{3}J(H,H)=8.2 Hz, 2H; HC_{ArNH2}) 7.98 (AA'BB', ^{3}J(H,H)=8.2 Hz, 2H; HC_{ArNH2}), 8.72–8.76 (m, 6H; HC^{β}), 8.83 (AB, ^{3}J(H,H)=4.7 Hz, 2H; HC^{β}); ^{13}C NMR ($CDCl_3$, 100 MHz): *δ*=55.6, 56.1 (CH_3), 90.9, 91.0, 110.3, 111.2. 113.0, 113.2, 113.3, 119.3, 130.4 (br s), 133.0, 135.4, 145.7, 161.2, 161.7 (C_{Ar}); IR (KBr): $\tilde{\nu}$=3320 (NH), 3394, 3474 cm^{-1} (NH_2); HRMS (ESI): *m*/*z*: calcd for $C_{53}H_{50}N_5O_9^+$, 900.3603 $[M+H]^+$; found 900.3599.

General procedure for the synthesis of aziridines 14. A mixture of amino-porphyrin **12** (1 eq), alkyl glyoxylate **3** (1.33 eq) and anhydrous Na_2SO_4 (100 mg) in dry benzene (10 ml) was stirred at ambient temperature until completion of the reaction (controlled by TLC, observed reaction times are reported below). Sodium sulfate was filtered off and the solvent was removed *in vacuo*. The residue was dissolved in dry 1,4-dioxane (2 ml) and 3 droplets of boron trifluoride etherate were added. A solution of alkyl diazoacetate **4** (1.33 eq) in 1,4-dioxane (0.5 ml) was added dropwise and the mixture was stirred for another 2.5 h and quenched with 5 droplets of triethylamine. The mixture was diluted with water, extracted with DCM and dried over Na_2SO_4. The desiccant was filtered off, the solvent was removed *in vacuo* and the residue was separated by column chromatography (silica gel, $CHCl_3$) to afford products as violet crystals.

Diethyl *cis*-1-{4-[10,15,20-tris(4-bromophenyl)porphyrin-5-yl]phenyl}aziridine-2,3-dicarboxylate (14ba). Reaction time: 50 min. Yield: 70% (20.2 mg, 0.020 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz): δ=-2.82 (s, 2H; NH), 1.45 (t, ^3J(H,H)=7.1 Hz, 6H; CH_3), 3.50 (s, 2H; HC_{az}), 4.43 (q, ^3J(H,H)=7.1 Hz, 4H; CH_2), 7.46 (AA'BB', ^3J(H,H)=8.4 Hz, 2H; HC_{ArN}), 7.90 (AA'BB', 6H, HC_{Ar}), 8.06–8.08 (m, 6H; HC_{Ar}), 8.12 (AA'BB', ^3J(H,H)=8.4 Hz, 2H; HC_{ArN}), 8.83–8.86 (m, 8H; HC^{β}); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=14.2 (CH_3), 43.3 (C_{Az}), 62.0 (CH_2), 118.5, 118.7, 118.8, 120.0, 122.6, 129.9, 130.0, 131.1 (br s), 131.3, 135.2, 135.8, 137.8, 140.87, 140.89, 150.5 (C_{Ar}), 167.0 (C=O); IR (KBr): $\tilde{\nu}$=3316 (N-H), 1703 cm^{-1} (C=O); UV/Vis (PhCN): λ_{max} (lg ε)=424 (5.24), 486 (3.24), 518 (3.87), 553 (3.64), 593 (3.38), 650 nm (3.38); HRMS (ESI): *m*/*z*: calcd for $C_{52}H_{39}Br_3N_5O_4^+$, 1034.0547 $[M+H]^+$; found 1034.0555.

Diethyl *cis*-1-{4-[10,15,20-tris(4-(trifluoromethyl)phenyl)porphyrin-5-yl]phenyl}aziridine-2,3-dicarboxylate (14ca). Reaction time: 50 min. Yield: 52% (11.6 mg, 0.012 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz): δ=-2.81 (s, 2H; NH), 1.44 (t, ^3J(H,H)=7.1 Hz, 6H; CH_3), 3.49 (s, 2H; HC_{az}), 4.42 (q, ^3J(H,H)=7.1 Hz, 4H; CH_2), 7.47 (AA'BB', ^3J(H,H)=8.4 Hz, 2H; HC_{ArN}), 8.05 (AA'BB', ^3J(H,H)=8.0 Hz, 6H; HC_{Ar}), 8.13 (AA'BB', ^3J(H,H)=8.4 Hz, 2H; HC_{ArN}), 8.35 (AA'BB', ^3J(H,H)=8.0 Hz, 6H; HC_{Ar}), 8.80–8.81 (m, 6H, HC^{β}), 8.86 (AB, ^3J(H,H)=4.9 Hz, 2H; HC^{β}); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=14.2 (CH_3), 43.3 (C_{Az}), 62.1 (CH_2), 118.5, 118.6, 118.8, 120.4, 123.8 (q, ^4J(C,F)=3.7 Hz), 124.5 q (^1J(C,F)=272 Hz), 130.3 q (^3J(C,F)=32.5 Hz), 131.4 (br s), 134.6, 135.2, 137.6, 145.6, 150.6 (C_{Ar}), 167.0 (C=O); IR (KBr): $\tilde{\nu}$=3447

(N-H), 1712 cm^{-1} (C=O); UV/Vis (PhCN): λ_{max} (lg ε)=423 (5.11), 486 (3.05), 517 (3.78), 553 (3.46), 593 (3.25), 650 nm (3.19); HRMS (ESI): *m*/*z*: calcd for $C_{55}H_{39}F_9N_5O_4^+$, 1004.2853 $[M+H]^+$; found 1004.2824.

Diethyl *trans*-1-{4-[10,15,20-tris(4-(trifluoromethyl)phenyl)porphyrin-5-yl]phenyl}aziridine-2,3-dicarboxylate (*trans*-14ca). Yield: 10% (2.0 mg, 0.002 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz): δ=-2.81 (s, 2H; NH), 1.39 (t, ^3J(H,H)=7.1 Hz, 6H; CH_3), 3.76 (s, 2H; HC_{az}), 4.30-4.40 (m, 4H; CH_2), 7.82 (AA'BB', ^3J(H,H)=8.5 Hz, 2H; HC_{ArN}), 8.05 (AA'BB', ^3J(H,H)=8.0 Hz, 6H; HC_{Ar}), 8.09 (AA'BB', ^3J(H,H)=8.5 Hz, 2H; HC_{ArN}), 8.35 (AA'BB', ^3J(H,H)=8.0 Hz, 6H; HC_{Ar}), 8.79 (AB, ^3J(H,H)=4.6 Hz, 2H; HC^{β}), 8.81 (s, 4H, HC^{β}), 8.87 (AB, ^3J(H,H)=4.6 Hz, 2H; HC^{β}); HRMS (ESI): *m*/*z*: calcd for $C_{55}H_{39}F_9N_5O_4^+$, 1004.2853 $[M+H]^+$; found 1004.2857.

Diethyl *cis*-1-{4-[10,15,20-tris(4-methylphenyl)porphyrin-5-yl]phenyl}aziridine-2,3-dicarboxylate (14da). Reaction time: 4 h. Yield: 78% (25.4 mg, 0.030 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz): δ=-2.77 (s, 2H; NH), 1.43 (t, ^3J(H,H)=7.1 Hz, 6H; CH_3), 2.72 (s, 9H; $ArCH_3$), 3.48 (s, 2H; HC_{Az}), 4.41 (q, ^3J(H,H)=7.1 Hz, 4H; CH_2), 7.44 (AA'BB', ^3J(H,H)=8.4 Hz, 2H; HC_{ArN}), 7.56 (AA'BB', ^3J(H,H)=7.8 Hz, 6H; HC_{Ar}), 8.09–8.13 (m, 2H+6H; HC_{ArN} + HC_{Ar}), 8.78 (AB, ^3J(H,H)=4.9 Hz, 2H; HC^{β}), 8.86–8.88 (m, 6H; HC^{β}); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=14.2 (CH_3), 21.5 ($ArCH_3$), 43.2 (C_{az}), 62.0 (CH_2), 118.4, 119.0, 120.2, 120.3, 127.4, 130.7 (br s), 131.2, 134.5, 135.2, 137.32, 137.33, 138.2, 139.21, 139.23, 150.2, (C_{Ar}) 167.0 (C=O); IR (KBr): $\tilde{\nu}$=3316 (N-H), 1736 cm^{-1} (C=O); UV/Vis (PhCN): λ_{max} (lg ε)=424 (5.50), 486 (3.51), 518 (4.10), 555 (3.92), 594 (3.62), 650 nm (3.63); HRMS (ESI): *m*/*z*: calcd for $C_{55}H_{48}N_5O_4^+$, 842.3701 $[M+H]^+$; found 842.3690.

Diethyl *cis*-1-{4-[10,15,20-tris(4-methoxyphenyl)porphyrin-5-yl]phenyl}aziridine-2,3-dicarboxylate (14ea). Reaction time: 24 h. Yield: 58% (24.3 mg, 0.028 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz): δ=-2.71 (s, 2H; NH), 1.45 (t, ^3J(H,H)=7.1 Hz, 6H; CH_3), 3.49 (s, 2H; HC_{Az}), 4.095 (s, 3H; OCH_3), 4.098 (s, 6H, OCH_3), 4.43 (q, ^3J(H,H)=7.1 Hz, 4H; CH_2), 7.29 (AA'BB', ^3J(H,H)=8.5 Hz, 6H; HC_{Ar}), 7.46 (AA'BB', ^3J(H,H)=8.2 Hz, 2H; HC_{ArN}), 8.12–8.15 (m, 2H+6H; HC_{ArN} + HC_{Ar}), 8.81 (AB, ^3J(H,H)=4.7 Hz, 2H; HC^{β}), 8.89–8.90 (m, 6H, HC^{β}); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=14.2 (CH_3), 43.3 (C_{az}), 55.5 (OCH_3), 62.0 (CH_2), 112.19, 112.20, 118.4, 119.0, 119.8, 120.0, 130.5, 131.0 (br s), 134.6, 135.2, 135.6, 138.2, 146.6 (br s), 150.3, 159.4 (C_{Ar}), 167.0 (C=O); IR (KBr): $\tilde{\nu}$=3316 (N-H), 1742 cm^{-1} (C=O); UV/Vis

(PhCN): λ_{max} (lg ε)=428 (4.89), 490 (2.95), 523 (3.48), 563 (3.48), 598 (3.03), 657 nm (3.20); HRMS (ESI): calcd for $C_{55}H_{48}N_5O_7^+$, 890.3548 $[M+H]^+$; found 890.3518.

Diethyl *trans*-1-{4-[10,15,20-tris(4-methoxyphenyl)porphyrin-5-yl]phenyl}aziridine-2,3-dicarboxylate (*trans*-14ea). Yield: 12% (5.0 mg, 0.006 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz): δ=-2.75 (s, 2H; NH), 1.39 (t, ^3J(H,H)=7.2 Hz, 6H; CH_3), 3.76 (s, 2H; HC_{Az}), 4.11 (s, 9H; OCH_3), 4.30-4.40 (m, 4H; CH_2), 7.30 (AA'BB', ^3J(H,H)=8.3 Hz, 6H; HC_{Ar}), 7.31 (AA'BB', ^3J(H,H)=8.2 Hz, 2H; HC_{ArN}), 8.10 (AA'BB', ^3J(H,H)=8.2 Hz, 2H; HC_{ArN}), 8.13 (AA'BB', ^3J(H,H)=8.3 Hz, 6H; HC_{Ar}), 8.81 (AB, ^3J(H,H)=4.9 Hz, 2H; HC^{β}), 8.85–8.90 (m, 6H; HC^{β}).

Diethyl *cis*-1-{4-[10,15,20-tris(2,4,6-trimethoxyphenyl)porphyrin-5-yl]phenyl}aziridine-2,3-dicarboxylate (14fa). Reaction time: 24 h. Yield: 9% (2 mg, 0.002 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz): δ=-2.61 (s, 2H; NH), 1.43 (t, ^3J(H,H)=7.1 Hz, 6H; CH_3), 3.45 (s, 2H; HC_{az}), 3.49 (s, 12H; OCH_3), 3.51 (s, 6H; OCH_3), 4.10 (s, 9H; OCH_3), 4.40 (q, ^3J(H,H)=7.1 Hz, 4H; CH_2), 6.57 (s, 6H; HC_{Ar}), 7.38 (AA'BB', ^3J(H,H)=8.3 Hz, 2H; HC_{ArN}), 8.09 (AA'BB', ^3J(H,H)=8.3 Hz, 2H; HC_{ArN}), 8.68 (AB, ^3J(H,H)=4.7 Hz, 2H; HC^{β}), 8.72 (AB, ^3J(H,H)=4.7 Hz, 2H; HC^{β}), 8.75 (AB, ^3J(H,H)=4.7 Hz, 2H; HC^{β}), 8.76 (AB, ^3J(H,H)=4.7 Hz, 2H; HC^{β}); HRMS (ESI): *m*/*z*: calcd for $C_{61}H_{60}N_5O_{13}^+$, 1070.4182 $[M+H]^+$; found 1070.4150.

Dibutyl *cis*-1-{4-[10,15,20-tris(4-methylphenyl)porphyrin-5-yl]phenyl}aziridine-2,3-dicarboxylate (14db). Reaction time: 4 h. Yield: 49% (53.1 mg, 0.059 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz): δ=-2.78 (s, 2H; NH), 1.06 (t, ^3J(H,H)=7.3 Hz, 6H; CH_3), 1.50 – 1.59 (m, 4H; CH_2), 1.79 – 1.86 (m, 4H; CH_2), 2.73 (s, 9H, $ArCH_3$), 3.51 (s, 2H, HC_{az}), 4.38 (t, ^3J(H,H)=6.7 Hz, 4H; O-CH_2), 7.45 – 7.49 (m, 2H; HC_{ArN}), 7.58 (AA'BB', ^3J(H,H)=7.8 Hz, 6H; HC_{Ar}), 8.14 (AA'BB', ^3J(H,H)=7.8 Hz, 6H; HC_{Ar}), 8.16 – 8.18 (m, 2H; HC_{ArN}), 8.84 (AB, ^3J(H,H)=4.7 Hz, 2H; HC^{β}), 8.89 – 8.93 (m, 6H; HC^{β}); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=13.7, 19.1, 21.5, 30.6, 43.3, 65.9, 118.4, 119.0, 120.2, 120.3, 127.4, 130.9, 131.0 (br. s.), 134.5, 135.2, 137.31, 137.33, 138.2, 139.2, 139.3, 146.2 (br. s.), 150.4, 167.1; IR ($CHCl_3$): $\tilde{\nu}$=3320 (N-H), 1745 cm^{-1} (C=O); HRMS (ESI): *m*/*z*: calcd for $C_{59}H_{56}N_5O_4^+$, 898.4327 $[M+H]^+$; found 898.4335.

Dihexyl *cis*-1-{4-[10,15,20-tris(4-methylphenyl)porphyrin-5-yl]phenyl}aziridine-2,3-dicarboxylate (14dc). Reaction time: 4 h. Yield: 79% (36.0 mg, 0.04 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz): δ=-2.70 (s, 2H; NH), 0.99 (t, ^3J(H,H)=7.0 Hz, 6H; CH_3), 1.40 – 1.45 (m, 8H; $CH_3(CH_2)_2$), 1.45 – 1.55 (m, 4H; $CH_2(CH_2)_2O$), 1.79 – 1.88 (m, 4H; CH_2CH_2O), 2.74 (s, 9H, $ArCH_3$), 3.51 (s, 2H, HC_{az}), 4.37 (t,

^3J(H,H)=6.9 Hz, 4H; OC$\underline{H}_2$), 7.47 (AA'BB', ^3J(H,H)=8.2 Hz, 2H; $\underline{H}C_{ArN}$), 7.58 (AA'BB', ^3J(H,H)=7.7 Hz, 6H; $\underline{H}C_{Ar}$), 8.14 (AA'BB', ^3J(H,H)=7.7 Hz, 6H; $\underline{H}C_{Ar}$), 8.16 (AA'BB', ^3J(H,H)=8.2 Hz, 2H; $\underline{H}C_{ArN}$), 8.84 (AB, ^3J(H,H)=4.7 Hz, 2H; $\underline{H}C^{\beta}$), 8.89 – 8.93 (m, 6H; $\underline{H}C^{\beta}$); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=14.0, 21.5, 22.6, 25.5, 28.5, 31.5, 43.3, 66.2, 118.4, 119.0, 120.2, 120.3, 127.4, 131.0 (br. s.), 134.5, 135.2, 137.31, 137.33, 138.2, 139.2, 139.3, 150.4, 167.1; IR (KBr): $\tilde{\nu}$=3317 (N-H), 1752, 1736 cm^{-1} (C=O); HRMS (ESI): *m*/*z*: calcd for $C_{63}H_{64}N_5O_4^+$, 954.4953 $[M+H]^+$; found 954.4974.

Dioctyl *cis*-1-{4-[10,15,20-tris(4-methylphenyl)porphyrin-5-yl]phenyl}aziridine-2,3-dicarboxylate (14dd). Reaction time: 4 h. Yield: 83% (23 mg, 0.022 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz): δ=-2.76 (s, 2H; N$\underline{H}$), 0.92 (t, ^3J(H,H)=6.8 Hz, 6H; C$\underline{H}_3$), 1.30 – 1.40 (m, 20H; C$\underline{H}_2$), 1.77 – 1.84 (m, 4H; C$\underline{H}_2$), 2.72 (s, 9H; ArC$\underline{H}_3$), 3.48 (s, 2H, $\underline{H}C_{az}$), 4.34 (t, ^3J(H,H)=6.9 Hz, 4H; O-C$\underline{H}_2$), 7.42 – 7.46 (m, 2H; $\underline{H}C_{ArN}$), 7.57 (AA'BB', ^3J(H,H)=7.8 Hz, 6H; $\underline{H}C_{Ar}$), 8.11 (AA'BB', ^3J(H,H)=7.8 Hz, 6H; $\underline{H}C_{Ar}$), 8.12 – 8.16 (m, 2H; $\underline{H}C_{ArN}$), 8.80 (AB, ^3J(H,H)=4.7 Hz, 2H; $\underline{H}C^{\beta}$), 8.87 – 8.91 (m, 6H; $\underline{H}C^{\beta}$); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=14.1, 21.5, 22.6, 25.9, 28.6, 29.20, 29.25, 31.8, 43.3, 66.2, 118.4, 119.0, 120.2, 120.3, 127.4, 130.9, 131.1 (br. s.), 134.5, 135.2, 137.32, 137.34, 138.2, 139.2, 139.3, 150.4, 167.1; HRMS (ESI): *m*/*z*: calcd for $C_{67}H_{72}N_5O_4^+$, 1010.5579 $[M+H]^+$; found 1010.5595.

General procedure for porphyrin-fullerene dyads 1. A solution of *cis*-aziridine **14** (1 eq) and fullerene C_{60} (2 eq) in chlorobenzene (2 ml) was stirred at 100 °C for 8 h. Reaction mixture was separated by column chromatography (silica gel, benzene) to afford product as purple-brown solid.

Dyad 1ba (Br, Et). Yield: 28% (4 mg, 0.002 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz): δ=-2.80 (s, 2H; N$\underline{H}$), 1.34 (t, ^3J(H,H)=7.1 Hz, 6H; C$\underline{H}_3$), 4.42–4.50 (m, 4H; C$\underline{H}_2$), 6.76 (s, 2H; $\underline{H}C_{Pyr}$), 7.71 (AA'BB', ^3J(H,H)=8.6 Hz, 2H; $\underline{H}C_{ArN}$), 7.92–7.96 (m, 6H, $\underline{H}$CAr), 8.09–8.13 (m, 6H, $\underline{H}C_{Ar}$), 8.31 (AA'BB', ^3J(H,H)=8.6 Hz, 2H; $\underline{H}C_{ArN}$), 8.86 (s, 4H; $\underline{H}C^{\beta}$), 8.88 (AB, ^3J(H,H)=4.7 Hz, 2H; $\underline{H}C^{\beta}$), 8.97 (AB, ^3J(H,H)=4.7 Hz, 2H; $\underline{H}C^{\beta}$); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=14.4 ($\underline{C}H_3$), 62.2 ($\underline{C}H_2$), 71.0 ($\underline{C}^q$), 74.7 ($\underline{C}$H), 117.1, 118.8, 118.9, 120.4, 122.60, 122.62, 130.00, 130.03, 131.2 (br s), 135.6, 135.8, 135.86, 135.90, 136.7, 139.4, 139.9, 140.97, 141.01, 141.4, 141.5 (2C), 141.6, 141.77, 141.80, 142.2, 142.4, 142.7, 142.8 (2C), 144.0, 144.1, 144.9, 145.0, 145.2, 145.3, 145.35, 145.38, 145.41, 145.76, 145.80, 145.9, 146.1, 147.2, 150.1, 153.0 ($\underline{C}_{Ar}$), 170.2 (C=O); IR ($CHCl_3$): $\tilde{\nu}$=3307 (N-H), 1733 cm^{-1} (C=O);

UV/Vis (PhCN): λ_{max} (lg ε)=425 (5.53), 489 (3.76), 518 (4.22), 555 (4.02), 593 (3.72), 651 nm (3.64); HRMS (ESI): *m*/*z*: calcd for $C_{112}H_{39}Br_3N_5O_4^+$, 1754.0547 $[M+H]^+$; found 1754.0492.

Dyad 1ca (CF_3, Et). Yield: 21% (5 mg, 0.003 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz): δ=-2.77 (s, 2H; NH), 1.34 (t, ^3J(H,H)=7.1 Hz, 6H; C$\underline{H}_3$), 4.42-4.50 (m, 4H; C$\underline{H}_2$), 6.77 (s, 2H; $\underline{H}C_{Pyr}$), 7.73 (AA'BB', ^3J(H,H)=8.5 Hz, 2H; $\underline{H}C_{ArN}$), 8.07-8.10 (m, 6H; $\underline{H}C_{Ar}$), 8.33 (AA'BB', ^3J(H,H)=8.5 Hz, 2H; $\underline{H}C_{ArN}$), 8.36-8.40 (m, 6H; $\underline{H}C_{Ar}$), 8.83–8.85 (m, 6H; $\underline{H}C^{\beta}$), 9.01 (d, ^3J(H,H)=4.6 Hz, 2H; $\underline{H}C^{\beta}$); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=14.4 ($\underline{C}H_3$), 62.2 ($\underline{C}H_2$), 71.0 ($\underline{C}^q$), 74.7 ($\underline{C}H$), 96.1, 117.1, 118.5, 118.8, 120.8, 123.8, 124.5 (q, ^1J(C,F)=272 Hz), 130.3 (q, ^3J(C,F)=32.5 Hz), 131.3 (br s), 134.6, 135.4, 135.7, 135.9, 136.7, 139.4, 139.9, 141.46, 141.50, 141.6, 141.79, 141.82, 142.3, 142.4, 142.7, 142.8, 144.1, 144.2, 144.9, 145.0, 145.2, 145.3, 145.38, 145.41, 145.42, 145.5, 145.68, 145.72, 145.79, 145.83, 145.9, 146.1, 147.2, 150.1, 153.0 ($\underline{C}_{Ar}$), 170.2 (C=O); IR ($CHCl_3$): $\tilde{\nu}$=3313 (N-H), 1736 cm^{-1} (C=O); UV/Vis (PhCN): λ_{max} (lg ε)=424 (5.89), 487 (4.12), 518 (4.61), 553 (4.36), 593 (4.14), 649 nm (4.01); HRMS (ESI): *m*/*z*: calcd for $C_{115}H_{39}F_9N_5O_4^+$, 1724.2853 $[M+H]^+$; found 1724.2843.

Dyad 1da (CH_3, Et). Yield: 42% (17 mg, 0.011 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz): δ=-2.73 (s, 2H; N$\underline{H}$), 1.35 (t, ^3J(H,H)=7.1 Hz, 6H; C$\underline{H}_3$), 2.73 (s, 6H; ArC$\underline{H}_3$), 2.74 (s, 3H; ArC$\underline{H}_3$), 4.42–4.50 (m, 4H; C$\underline{H}_2$), 6.78 (s, 2H; $\underline{H}C_{Pyr}$), 7.58–7.61 (m, 6H, $\underline{H}$CAr), 7.71 (AA'BB', ^3J(H,H)=8.6 Hz, 2H; $\underline{H}C_{ArN}$), 8.12–8.15 (m, 6H, $\underline{H}$CAr), 8.33 (AA'BB', ^3J(H,H)=8.6 Hz, 2H; $\underline{H}C_{ArN}$), 8.88 (s, 4H; $\underline{H}C^{\beta}$) 8.91 (AB, ^3J(H,H)=4.7 Hz, 2H; $\underline{H}C^{\beta}$), 8.94 (AB, ^3J(H,H)=4.7 Hz, 2H; $\underline{H}C^{\beta}$); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=14.4 ($\underline{C}H_3$), 21.5 (Ar$\underline{C}H_3$), 62.2 ($\underline{C}H_2$), 71.0 ($\underline{C}^q$), 74.7 ($\underline{C}H$), 117.0, 119.4, 120.2, 120.3, 127.4, 130.9, 131.2 (br s), 134.5, 134.6, 135.6, 136.0, 136.1, 136.8, 137.4 (2C), 139.3 (2C), 139.5, 139.9, 141.5, 141.57 (2C), 141.64, 141.9, 142.3, 142.5, 142.8, 144.15, 144.23, 145.0, 145.1, 145.2, 145.3, 145.41, 145.45 (2C), 145.5, 145.8, 145.9, 146.0, 146.2, 147.3, 150.2, 153.1 ($\underline{C}_{Ar}$), 170.3 (C=O); IR ($CHCl_3$): $\tilde{\nu}$=3316 (N-H), 1733 cm^{-1} (C=O); UV/Vis (PhCN): λ_{max} (lg ε)= 425 (5.05), 487 (3.40), 519 (3.74), 556 (3.61), 595 (3.33), 651 nm (3.29); HRMS (ESI): *m*/*z*: calcd for: $C_{115}H_{48}N_5O_4^+$, 1562.3701 $[M+H]^+$; found 1562.3728.

Dyad 1ea (OMe, Et). Yield: 27% (10.2 mg, 0.007 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz): δ=-2.72 (s, 2H; NH), 1.33 (t, ^3J(H,H)=7.1 Hz, 6H; C$\underline{H}_3$), 4.12 (s, 6H; OCH_3), 4.13 (s, 3H; OCH_3), 4.41–4.49 (m, 4H; C$\underline{H}_2$), 6.74 (s, 2H; $\underline{H}C_{Pyr}$), 7.31–7.35 (m, 6H, $\underline{H}$CAr), 7.71 (AA'BB', ^3J(H,H)=8.6 Hz, 2H; $\underline{H}C_{ArN}$), 8.15 (AA'BB', ^3J(H,H)=8.6 Hz, 4H; $\underline{H}C_{Ar}$), 8.18 (AA'BB', ^3J(H,H)=8.6 Hz, 2H, $\underline{H}$CAr), 8.32 (AA'BB',

^{3}J(H,H)=8.6 Hz, 2H; HC_{ArN}), 8.89 (AB, ^{3}J(H,H)=4.6 Hz, 2H; HC^{β}), 8.90 (AB, ^{3}J(H,H)=4.6 Hz, 2H; HC^{β}), 8.91 (AB, ^{3}J(H,H)=4.6 Hz, 2H; HC^{β}), 8.93 (AB, ^{3}J(H,H)=4.6 Hz, 2H; HC^{β}); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=14.4 (CH_3), 55.6 (ArOCH_3), 62.1 (CH_2), 71.0 (C^{q}), 74.7 (CH), 112.26, 112.27, 117.0, 119.4, 119.9, 120.0, 131.1 (br s), 134.69, 134.71, 135.57, 135.61, 135.8, 136.1, 136.6, 139.3, 139.7, 141.3, 141.35, 141.40, 141.42, 141.6, 141.7, 142.1, 142.3, 142.6, 143.9, 144.0, 144.8, 144.9, 145.0, 145.18, 145.21, 145.3, 145.4, 145.6, 145.67, 145.73, 146.0, 147.1, 150.1, 152.9, 159.4 (C_{Ar}), 170.3 (C=O); IR (KBr): $\tilde{\nu}$=3316 (N-H), 1733 cm^{-1} (C=O). UV/Vis (PhCN): λ_{max} (lg ε)=427 (5.67), 491 (3.85), 521 (4.26), 559 (4.20), 596 (3.79), 654 nm (3.85); HRMS (ESI): *m*/*z*: calcd for $C_{115}H_{48}N_5O_7^+$, 1610.3548 $[M+H]^+$; found 1610.3547.

Dyad 1db (CH_3, Bu). Yield: 48% (39.1 mg, 0.024 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz): δ=-2.72 (s, 2H; NH), 0.92 (t, ^{3}J(H,H)=7.4 Hz, 6H; CH_3), 1.40 – 1.48 (m, 4H; CH_2), 1.65 – 1.77 (m, 4H; CH_2), 2.74 (s, 9H; ArCH_3), 4.33 – 4.44 (m, 4H; O-CH_2), 6.79 (s, 2H, HC_{Pyr}), 7.59 (AA'BB', ^{3}J(H,H)=7.3 Hz, 6H; HC_{Ar}), 7.70 (m, 2H; HC_{ArN}), 8.11 – 8.16 (m, 6H; HC_{Ar}), 8.32 – 8.34 (m, 2H; HC_{ArN}), 8.89 (s, 4H; HC^{β}), 8.92 (AB, ^{3}J(H,H)=4.7 Hz, 2H; HC^{β}), 8.95 (AB, ^{3}J(H,H)=4.7 Hz, 2H; HC^{β}); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=13.7, 19.2, 21.5, 30.6, 65.9, 71.0, 74.8, 116.9, 119.4, 120.2, 127.4, 130.7, 130.0 (br. s.), 134.5, 135.6, 135.9, 136.1, 136.6, 137.3, 139.35, 139.41, 139.8, 141.4, 141.48, 141.50, 141.70, 141.72, 142.2, 142.3, 142.6, 144.0, 144.1, 144.8, 144.9, 145.16, 145.18, 145.3, 145.4, 145.6, 145.7, 145.8, 146.0, 147.1, 150.2, 153.0, 170.5; IR (KBr): $\tilde{\nu}$=3320 (N-H), 1731 cm^{-1} (C=O); HRMS (ESI): *m*/*z*: calcd for $C_{119}H_{56}N_5O_4^+$, 1618.4327 $[M+H]^+$; found 1618.4378.

Dyad 1dc (CH_3, Hex). Yield: 47% (27 mg, 0.016 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz): δ=-2.69 (s, 2H; NH), 0.82 (t, ^{3}J(H,H)=7.2 Hz, 6H; CH_3), 1.20 – 1.35 (m, 8H; CH_2), 1.35 – 1.46 (m, 4H; CH_2), 1.68 – 1.78 (m, 4H; CH_2), 2.75 (s, 9H; ArCH_3), 4.32 – 4.45 (m, 4H; O-CH_2), 6.81 (s, 2H, HC_{Pyr}), 7.58-7.63 (m, 6H; HC_{Ar}), 7.72 (AB, ^{3}J(H,H)=8.5 Hz, 2H; HC_{ArN}), 8.11 – 8.18 (m, 6H; HC_{Ar}), 8.34 (AB, ^{3}J(H,H)=8.5 Hz, 2H; HC_{ArN}), 8.90 (s, 4H; HC^{β}), 8.93 (AB, ^{3}J(H,H)=4.8 Hz, 2H; HC^{β}), 8.97 (AB, ^{3}J(H,H)=4.8 Hz, 2H; HC^{β}); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=14.0, 21.5, 22.6, 25.8, 28.7, 31.4, 66.3, 71.1, 74.9, 117.0, 119.4, 120.2, 127.4, 131.0 (br. s.), 134.5, 135.6, 136.1, 136.8, 137.3, 139.3, 139.6, 140.0, 141.55, 141.66, 141.69, 141.9, 142.4, 142.5, 142.9, 144.2, 144.3, 145.0, 145.1, 145.2, 145.4, 145.5, 145.9, 146.1, 146.2,

147.3, 150.4, 153.1, 170.5; IR (KBr): $\tilde{\nu}$=3310 (N-H), 1756, 1730 cm^{-1} (C=O). HRMS (ESI): *m*/*z*: calcd for $C_{123}H_{37}N_5O_4^+$: 1674.4953, $[M+H]^+$; found 1674.5090.

Dyad 1dd (CH_3, Oct). Yield: 41% (34 mg, 0.020 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz): δ=-2.69 (s, 2H; NH), 0.77 (t, ^3J(H,H)=7.0 Hz, 6H; CH_3), 1.10 – 1.27 (m, 12H; CH_2), 1.27 – 1.36 (m, 4H; CH_2), 1.36 – 1.47 (m, 4H; CH_2), 1.67 – 1.78 (m, 4H; CH_2), 2.75 (s, 9H; ArCH_3), 4.32 – 4.46 (m, 4H; O-CH_2), 6.79 (s, 2H, HC_{Pyr}), 7.58-7.64 (m, 6H; HC_{Ar}), 7.71 (AB, ^3J(H,H)=8.3 Hz, 2H; HC_{ArN}), 8.11 – 8.16 (m, 6H; HC_{Ar}), 8.34 (AB, ^3J(H,H)=8.3 Hz, 2H; HC_{ArN}), 8.89 (s, 4H; HC^{β}), 8.93 (AB, ^3J(H,H)=4.7 Hz, 2H; HC^{β}), 8.96 (AB, ^3J(H,H)=4.7 Hz, 2H; HC^{β}); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=14.0, 21.5, 22.6, 26.1, 28.7, 29.2, 29.3, 31.7, 66.3, 71.1, 74.9, 116.9, 119.4, 120.2, 127.4, 130.9 (br. s.), 134.5, 135.6, 136.1, 136.7, 137.3, 139.3, 139.5, 140.0, 141.5, 141.6, 141.7, 141.9, 142.4, 142.5, 142.8, 144.2, 144.3, 145.0, 145.1, 145.2, 145.3, 145.5, 145.8, 146.1, 146.2, 147.2, 150.4, 153.1, 170.5; IR (KBr): $\tilde{\nu}$=3320 (N-H), 1732 cm^{-1} (C=O). HRMS (ESI): *m*/*z*: calcd for $C_{127}H_{72}N_5O_4^+$: 1730.5579, $[M+H]^+$; found 1730.5503.

Supporting Information available: ^{1}H- and ^{13}C-NMR spectra of new compounds, ^{1}H-^{1}H NOESY spectrum of compound *trans*-**5ab**, ^{1}H-^{13}C HMBC spectra of compounds *cis*-**5ab** and *cis*-**5bb**, ^{1}H-^{13}C HSQC spectrum of compound *cis*-**5ab**.

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