## Donor-substituted peralkynylated "radiaannulenes": novel all-carbon macrocycles with an intense intramolecular charge-transfer

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Scheme S1: Synthesis of monocycles 1–3; *Reagents and conditions*: i, CuCl, TMEDA, O<sub>2</sub>, acetone, r.t., 2 h, 57 % (6), 32 % (7), 32 % (8); ii, Bu<sub>4</sub>NF, THF, 0 °C, 10 min; iii, CuCl, TMEDA, O<sub>2</sub>, acetone, r.t., 2 h, 48 % (1), 32 % (2), 14 % (3).



Scheme S2: Synthesis of bicycles 4 and 5; *Reagents and conditions*: i, CuCl, TMEDA, O<sub>2</sub>, acetone, r.t., 2 h, 29 % (9), 39 % (10); ii, Bu<sub>4</sub>NF, THF, 0 °C, 10 min; iii, CuCl, TMEDA, O<sub>2</sub>, acetone/PhH/THF 1:1:1, r.t., 2 h, 88 % (4), 16 % (5).

Experimental for 4: To a cooled (0 °C) solution of 9 (90 mg, 0.0328 mmol) in moist THF (20 ml), tetrabutylammonium fluoride (0.5 ml of a 1.0M solution in THF, 0.5 mmol) was added. After stirring for 10 min, TLC control indicated complete protodesilylation. CH<sub>2</sub>Cl<sub>2</sub> (100 ml) was added to the mixture, followed by filtration of the solution through a plug of SiO<sub>2</sub> (CH<sub>2</sub>Cl<sub>2</sub>). Removal of the volatiles *in vacuo* left a red oil that was redissolved in a mixture of acetone/PhH/THF 1:1:1 (450 ml). To this solution, Hav-catalyst (freshly prepared solution of CuCl (100 mg, 1.0 mmol) and TMEDA (0.15 ml, 116 mg, 1.0 mmol) in acetone (25 ml)) was added, and the mixture stirred for 2 h at room temperature. The deep brown solution was filtered through a plug of SiO<sub>2</sub> (acetone), followed by the removal of the solvents in vacuo. The residue was subjected to flash chromatography (hexane/EtOAc 20:1), yielding the product as a brown solid (61.5 mg, 88%). UV/Vis (CHCl<sub>3</sub>)  $\lambda$  408 (65400), 498 (122500), 595 (42300); FT-IR (CHCl<sub>3</sub>) v 3023, 2966, 2905, 2870, 2181, 1589, 1477, 1432, 1395, 1364, 1248, 879; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ1.25 (s, 72 H, CH<sub>3</sub>), 1.29 (s, 72 H, CH<sub>3</sub>), 7.36 (m, 20 H, CH), 7.43 (br t, ~4 H, CH);  $^{13}$ C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$ 31.29, 31.31, 34.82, 34.86, 84.14, 85.27, 86.01, 86.08, 87.03, 87.52, 90.85, 96.27, 103.25, 103.93, 114.61, 115.79, 120.82, 120.89, 121.47, 124.20, 124.37, 126.37, 126.42, 151.05, 151.06; FT-ICR-MALDI-MS (DCTB) m/z 2114 (100, M<sup>+</sup>); HR-FT-ICR-MALDI-MS (DCTB) m/z 2113.3166, calc. for C<sub>162</sub>H<sub>168</sub><sup>+</sup>: 2113.3146.



**Fig. S1**: HR-FT-ICR-MALDI mass spectrum of **4** (matrix: 2-[(2E)-3-(4-*tert*-butylphenyl)-2-methyl-prop-enylidene]malononitrile (DCTB)).



**Fig. S2**: Decoupled <sup>13</sup>C NMR spectrum of **4** in CDCl<sub>3</sub> (125 MHz, 298 K) featuring two signals for the  $C(CH_3)_3$ -carbons, two signals for the  $C(CH_3)_3$ -carbons and as expected 21 signals in the  $C(sp)/C(sp^2)$  region.



**Fig. S3**: Electronic absorption spectra of **2** in pure CHCl<sub>3</sub> (red), after acidification with PTSA (black) and after neutralisation with Et<sub>3</sub>N (blue).



**Fig. S4**: Electronic absorption spectra of **5** in pure CHCl<sub>3</sub> (red), after acidification with PTSA (black) and after neutralisation with Et<sub>3</sub>N (blue).



Fig. S5: Electronic absorption spectra of radiaannulene 2 (red), dehydroannulene 11 (blue) and expanded radialene 12 (black) in CHCl<sub>3</sub>.

## **Electrochemistry.**

Electrochemical investigations in  $CH_2Cl_2$  (Table S1) and in THF (Table S2) containing 0.1M  $Bu_4NPF_6$  as supporting electrolyte and on a glassy carbon working electrode gave for all species several reduction and oxidation steps. All oxidation steps observed for the studied species correspond to electron transfers on the N,N-dialkylaniline moieties, whereas the reductions occur on the conjugated core with the exception of species **3**, for which the third and fourth reduction steps occur on the nitrophenyl moieties.

**Experimental:** The electrochemical experiments were carried out at 20 °C in THF and  $CH_2Cl_2$  containing 0.1M Bu<sub>4</sub>NPF<sub>6</sub> in a classical three-electrode cell.  $CH_2Cl_2$  was purchased spectroscopic grade from Merck, dried over molecular sieves (4 Å) and stored under Argon prior to use. Bu<sub>4</sub>NPF<sub>6</sub> was purchased electrochemical grade from Fluka and used as received. THF was refluxed over sodium/benzophenone and distilled off before use. The working electrode was a glassy carbon disk electrode (3 mm in diameter) used either motionless for CV (0.1 to 10 Vs<sup>-1</sup>) or as rotating-disk electrode for rotating disk voltammetry (RDV). The auxiliary electrode was a platinum wire and the reference electrode was an aqueous Ag/AgCl electrode. All potentials are referenced to the ferrocene/ferrocinium (Fc/Fc<sup>+</sup>) couple used as an internal standard. The accessible range of potentials on the glassy carbon electrode was +1.4 to -2.4 V versus Fc/Fc<sup>+</sup> in CH<sub>2</sub>Cl<sub>2</sub>. The electrochemical cell was connected to a computerised multipurpose electrochemical device AUTOLAB (Eco Chemie BV, Utrecht, The Netherlands) controlled by the GPES software running on a personal computer.

	Cyclic Voltammetry			Rotating Disk Voltammetry	
	$E^{\rm o}/{ m V}^{\rm a}$	$\Delta E_{\rm p}/{ m mV}$	$E_{\rm p}/{ m V}^{\rm b}$	$E_{1/2}/V$	Slope /mV
1			+0.34	+0.34 (2 e <sup>-</sup> )	35
	-1.19	75		-1.27 (1 e <sup>-</sup> )	75
	-1.41	80		-1.52 (1 e <sup>-</sup> )	65
			-1.80	-1.98 (2 e <sup>-</sup> )	130
			-1.90		
			-2.17		
2			+0.55		
			+0.43		
			+0.36	+0.37	60
	-1.34	75		-1.34 (1 e <sup>-</sup> )	75
	-1.59	80		-1.64 (1 e <sup>-</sup> )	75
			-1.97		
			-2.12		
			-2.30		
3			+0.55		
			+0.41	с	
	-1.07	60		-1.11 (1 e <sup>-</sup> )	75
	-1.24	70		-1.28 (1 e <sup>-</sup> )	80
	-1.52	60		-1.56 (2 e <sup>-</sup> )	110
	-1.64	70			
			-1.94		
			-1.98		
			-2.08		
4	-0.81	85		-0.81	80
	-1.12	70		-1.12	80
	-1.45	70		с	
	-1.61	100			
5			+0.52		
			+0.45	$+0.54(4 e^{-})$	120
			+0.34	$+0.38(4 e^{-})$	60
	-0.98	100		-1.00(1  e)	80
	-1.29	100		-1.25(1  e)	(c)
	-1.67	90			

**Table S1.** Cyclic voltammetry and rotating disk voltammetry data in  $CH_2Cl_2$  (+ 0.1M $Bu_4NPF_6$ ): potentials vs.  $Fc/Fc^+$ . Working electrode: glassy carbon electrode; counterelectrode: Pt; reference electrode: Ag/AgCl. Scan rate: 0.1 V s^{-1}Cyclic VoltammetryRotating Disk Voltammetry

<sup>a</sup>  $E^{o} = (E_{pc} + E_{pa})/2$ , where  $E_{pc}$  and  $E_{pa}$  correspond to the cathodic and anodic peak potentials, respectively. <sup>b</sup>  $E_{p}$  = irreversible peak potential <sup>c</sup> Electrode inhibition during oxidation. No plateau limiting current could be observed.

	Cyclic voltammetry			Rotating Disk Voltammetry	
	$E^{\rm o}/~{ m V}^{\rm a}$	$\Delta E_{\rm p}/{ m mV}$	$E_{\rm p}/{ m V}^{ m b}$	$E_{1/2}/V$	Slope /mV
1			+0.34	+0.41 (2 e <sup>-</sup> )	60
				-1.22(1  e)	70
	-1.20	90		-1.53(1  e)	80
	-1.47	80	-1.86	-1.91	
			-1.94		
			-2.22		
2			+0.54	$+0.40(2 e^{-})$	80
			+0.38	$+0.28(2 e^{-})$	35
	-1.37	90		$-1.29(1 e^{-1})$	80
	-1.67	90		c	
			-1.85		
			-2.15		
3			+0.44	с	
-	-1.13	70	0	-1 12 (1 e <sup>-</sup> )	80
	-1.38	80		-1.38(1  e)	100
	-1.73	60		$-1.73(2 e^{-1})$	120
	_1.75	70		1.75 (20)	
	1.01		-2.33		
4	-0.83	100		-0.89	120
	-1 19	125		c	
	-1.62	125		-	
	-1.75	125			
5			+0.57		
			+0.48	+0.37 (8 e <sup>-</sup> )	80
	-0.99	80		$-1.00(1 e^{-})$	80
	-1.36	80		$-1.37(1 e^{-1})$	70
	-1.78	90		-1.87 (1 e <sup>-</sup> )	

**Table S2.** Cyclic voltammetry and rotating disk voltammetry data in THF (+ 0.1MBu<sub>4</sub>NPF<sub>6</sub>): potentials vs. Fc/Fc<sup>+</sup>. Working electrode: glassy carbon electrode; counterelectrode: Pt; reference electrode: Ag/AgCl. Scan rate:  $0.1 \text{ V s}^{-1}$ Cyclic VoltammetryRotating Disk Voltammetry

<sup>a</sup>  $E^{o} = (E_{pc} + E_{pa})/2$ , where  $E_{pc}$  and  $E_{pa}$  correspond to the cathodic and anodic peak potentials, respectively. <sup>b</sup>  $E_{p}$  = irreversible peak potential. <sup>c</sup> Unresolved waves.