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Supporting Information of

Extended Germa[N]pericyclynes: Synthesis and Characterization

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[1] General information

¹H and ¹³C NMR spectra were recorded using a JEOL JNM-ECP500 spectrometer (500 MHz for ¹H NMR and 126 MHz for ¹³C NMR) Chemical shifts are reported as δ values in ppm and calibrated with respect to the residual solvent peak (CDCl₃: δ 7.26 for ¹H NMR and δ 77.00 for ¹³C NMR; CD₂Cl₂: δ 5.32 for ¹H NMR and δ 53.84 for ¹³C NMR; *N*-R methyl-2-pyrrolidinone-d9: δ 2.85 for ¹H NMR of *N*-Me and δ 174.7 for ¹³C NMR of amido carbonyl) or tetramethylsilane (δ 0 for ¹H NMR). The abbreviations used are as follows: s (singlet), d (doublet), t (triplet), q (quartet), sept (septet), br (broad peak), and m (complex multiplet). Melting points were measured using a Yanaco Micro melting point apparatus. Infrared spectra were measured using a JASCO FT-IR-4200 spectrometer. Mass spectra were recorded using a JEOL JMS-700 MStaion [EI (70 eV), CI, FAB, and ESI], and Bruker Autoflex II (MALDI-TOF). UV-visible UV/visible spectra were recorded using JASCO V-630. Fluorescence spectra were collected using JASCO FP-6500. Low temperature phosphorescence emission spectra were recorded on a Horiba Jobin Yvon Fluoromax-4 spectrofluorometer. The cyclic voltammetry measurements of the compounds were performed using a BAS electrochemical analyser ALS612D in dichloromethane containing *n*-Bu₄NPF₆ as the supporting electrolyte at 298 K (100 mV s⁻¹). The glassy carbon working electrode was polished using BAS polishing alumina suspension and rinsed with water before use. The counter electrode was a platinum wire. The measured potentials were recorded with respect to Ag/AgNO₃ and normalized with respect to Fc/Fc⁺. Density Functional Theory (DFT) calculations were performed using the Gaussian09, and the geometries of the molecules were optimized by employing the B3LYP density functionals and the 6-31G(d,p) basis set in this series of calculations.

For preparation procedures and characterizations of germa[6]pericyclyne 8, see our previous work.¹



Extended germa[N]pericyclynes

[2] Bond lengths and angles from X-ray crystallographic analysis

 Table 1. Bond lengths and angles of extended germapericyclynes

 and their comparison to non-extended materials



germapericyclynes

germapericyclynes

Non-extende	e d [4]	[5]	[6]	[8]
-C≡C- (Å)	1.209(4)	1.218(11)	1.203(5)	1.205(4)
∠C-X-C(°)	103.7(1) 104.0(1)	105.8(3) 105.7(3) 104.1(3)	109.0(3) 110.5(3) 107.4(3)	105.96(10) 104.16(10) 108.06(11) 108.14(10)
∠X-C≡C(°)	171.0(2) 167.7(2)	178.6(6) 169.8(6) 175.4(8) 176.1(8) 170.2(8)	174.0(5) 171.8(5)	173.9(2) 170.9(2)
Extended	[4]	[5]	[6]	[8]
-C≡C- (Å)	1.208(6) 1.203(6)	1.196(5) 1.202(5)	1.201(7) 1.172(7)	1.188(10) 1.210(10)
∠C-X-C(°)	104.33(18)	98.55(15) 104 59(16)	104.1(2) 103.4(2)	104.3(3) 101.5(3)
		105.4(2)	106.7(2)	102.4(3) 106.8(3)

[3] UV-visible spectra



Compounds	Absorption maxima•nm (ε L•mol ⁻¹ •cm ⁻¹)				
Ext PhGe[5] (3)	248 (12800)	262 (12380)	270 (3380, sh),	278 (5310)	296 (250)
Ext PhGe[6] (4)	248 (14180)	262 (13640)	270 (3740, sh)	278 (6050)	294 (400)
Ext PhGe[7] (5)	248 (17500)	262 (16650)	270 (4700 sh)	278 (7080)	295 (390)
Ext PhGe[8] (6)	248 (25230)	262 (24050)	270 (6970, sh)	278 (9530)	294 (710)
PhGe[6] (9) ¹		261 (3064)			
TMS-CC-CC-TMS (10)	249 (610)	263 (920)		278 (850)	295 (350)

Fig S1. (a), (b) 0.1 mM in CH_2CI_2 except for **10** (1.0 M). Absorption spectrum of **9** is referred from our previous work.¹ (c) Plot of ϵ values of each absorption maxima against the number of Ph₂Ge-CC-CC units. Sh: Shoulder

[4] Fluorescence and phosphorescence emission spectra



Fig S2. (a) Fluorescence emission spectra (0.005 mM in CH_2CI_2 , $\lambda_{ex} = 262$ mn). (b) Phosphorescence emission spectra (0.1 mM in 2-methyltetrahydrofuran at 77 K, $\lambda_{ex} = 262$ mn, background cut off).

[5] Cyclic and differential pulse voltammetry

Fig S3. Cyclic and differential pulse voltammograms of extended germa[5]–,[6]–, [7]– and [8]pericyclynes **3–6** (1.0 mM in 0.1 M *n*-Bu₄NPF₆/CH₂Cl₂ solution)

[6] HOMO/LUMO orbitals and levels of extended octaphenyl germa[4]pericyclyne (2)

(Gaussian09, B3LYP/6-31G**, based on cif file)

LUMO+2		НОМО	
	-0.857 eV		-6.40 eV
LUMO+1		HOMO-1	
	-1.04 eV		-6.50 eV
LUMO		HOMO-2 (left) and HOMO-3 (right)	
	-1.39 eV		-6.54 eV

Fig S4. Frontier orbitals of acetylene and butadiyne compounds.

[7] Reference

(1) H. Tanimoto, T. Nagao, Y. Nishiyama, T. Morimoto, F. Iseda, Y. Nagato, T. Suzuka, K. Tsutsumi and K. Kakiuchi, *Dalton Trans.* 2014, **43**, 8338–8343.

(2) H. Tanimoto, T. Nagao, T. Fujiwara, Y. Nishiyama, T. Morimoto, T. Suzuka, K. Tsutsumi and K. Kakiuchi, *Dalton Trans.*, 2015, 44, 11811–11818.

(3) H. Tanimoto, T. Nagao, T. Fujiwara, T. Kakuta, K. Tanaka, Y. Chujo and K. Kakiuchi, *Polymer Chem.* 2015, **6**, 7495–7499.

in N-methyl-d3-pyrrolidinone-d6

DFILE	tf_02_004_Ph[4]_Proton-3-1.als
COMNT	single_pulse
DATIM	2016-02-08 23:28:58
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	16384
FREQU	9384.38 Hz
SCANS	8
ACQTM	1.7459 sec
PD	5.0000 sec
PW1	7.20 usec
IRNUC	1H
CTEMP	21.0 c
SLVNT	DMF-D7
EXREF	2.85 ppm
BF	0.10 Hz
RGAIN	30

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DFILE	tf_02_004_Ph[4]_Carbon-nmp1.als
COMNT	single pulse decoupled gated NOE
DATIM	2016-02-08 23:36:31
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	32767
FREQU	39308.18 Hz
SCANS	1302
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	4.00 usec
IRNUC	1H
CTEMP	21.5 c
SLVNT	DMF-D7
EXREF	174.70 ppm
BF	0.10 Hz
RGAIN	60

in CDCl₃

DELLE	tf 02 004 Ph[5] Proton-1-1 als
COMNT	single pulse
DATINA	2015 12 10 12 22 25
DATIN	2013-12-10 12:23:35
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13107
FREQU	7507.51 Hz
SCANS	8
ACQTM	1.7459 sec
PD	5.0000 sec
PW1	7.20 usec
IRNUC	1H
CTEMP	18.4 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.10 Hz
RGAIN	32

	tf_02_004_Ph[5]_Carbon-1-1.als
T	single pulse decoupled gated NOE
1	2015-12-10 12:25:25
C	13C
D	carbon.jxp
Q	125.77 MHz
Г	7.87 KHz
1	4.21 Hz
Г	26214
J	31446.54 Hz
S	1024
M	0.8336 sec
	2.0000 sec
	4.00 usec
2	1H
Ρ	17.6 c
Г	CDCL3
	77.00 ppm
	0.10 Hz
1	60

DFILE	tf_02_004_Ph[8]_Proton-1-1.als
COMNT	single_pulse
DATIM	2015-12-10 11:20:12
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13107
FREQU	7507.51 Hz
SCANS	8
ACQTM	1.7459 sec
PD	5.0000 sec
PW1	7.20 usec
IRNUC	1H
CTEMP	18.4 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.10 Hz
RGAIN	32

DFILE	tf_02_004_Ph[8]_Carbon-1-1.als
COMNT	single pulse decoupled gated NOE
DATIM	2015-12-10 11:21:60
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	1024
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	4.00 usec
IRNUC	1H
CTEMP	18.5 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.10 Hz
RGAIN	60

•Experimental and simulated isotopic patterns of extended germapericyclynes

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