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Electronic Supplementary Information

The ESI contains:

1	Syn	Synthetic Procedures2			
	1.1	General Synthetic Methods			
	1.2	Analytical Techniques			
	1.3	Synthesis of Compounds			
	1.4	Procedures for other Reactions			
2	NM	R Spectra10			
3	Sing	gle Crystal X-ray Diffraction Data18			
4	NM	R Monitoring Data20			
5	Stat	ionary Absorption Spectroscopy with Stepwise Illumination			
6	Qua	ntum Chemical Calculations22			
	6.1	Computational Investigation of the Light-induced Planar			
	1,2-Dij	phosphacyclubutadiene Formation (Part 1)22			
	6.2	Computational Analysis for Spectral Assignment (Part 2)			
	6.3	Computational Analysis for Energetic Considerations in the Dimerization Process			
	(Part 3))24			
	6.4	Electronic Structure and NMR calculations (Part 4)			
	6.5	Calculations of Aromaticity Parameters (Part 5)			

1 Synthetic Procedures

1.1 General Synthetic Methods

All reactions and product manipulations were carried out in flame-dried glassware under an inert atmosphere of argon using standard Schlenk-line or glovebox techniques (maintained at <0.1 ppm H₂O and <0.1 ppm O₂). (*t*BuCP)₂ was prepared according to a procedure previously reported in literature.¹ All other chemicals were purchased from commercial suppliers and used without further purification.

Solvents were dried and degassed with a MBraun SPS800 solvent purification system. Fluorobenzene was dried over sodium and distilled. All dry solvents except *n*-hexane were stored under argon over activated 3 Å molecular sieves in gas-tight ampoules. *n*-Hexane was instead stored over a potassium mirror.

Irradiation experiments for synthetic purposes were performed using a Hg-lamp (photoLAB reactor from UV-Consulting Peschl) or a chromatography lamp (from Herolab GmbH).

1.2 Analytical Techniques

NMR spectra were recorded on Bruker Avance 300 or 400 spectrometers at 300 K unless otherwise noted and internally referenced to residual solvent resonances (¹H NMR: C₆D₆: 7.16 ppm; ¹³C{¹H} NMR: C₆D₆: 128.06 ppm). Chemical shifts δ are given in ppm referring to external standards of tetramethylsilane (¹H, ¹³C{¹H}) or 85% phosphoric acid (³¹P and ³¹P{¹H} spectra). ¹H and ¹³C NMR signals were assigned based on 2D NMR spectra (¹H,¹H-COSY, ¹H,¹³C-HSQC, ¹H,¹³C-HMQC). Quantitative ³¹P NMR spectra were recorded as previously described.²

For GC-MS an Agilent 7820A GC system with mass detector 5977B was used with H₂ as carrier gas and a HP-5MS (30 m × 0.25 mm × 0.25 μ m) column. The standard heating procedure was as follows: 50°C \rightarrow 300°C. The GC analysis of the mixture of **3-endo** and **3-exo** is shown in Figure S1.



Figure S1. Chromatogram of mixture of **3-endo** and **3-exo**. The small peak at 9.978 could not be identified and the peak at 15.276 can be assigned to (*t*BuCP)₄ (**2**).



Figure S2. Mass spectrum of species arising in the chromatogram (Figure S1) at 14.281 min.



Figure S3. Mass spectrum of species arising in the chromatogram (Figure S1) at 14.458 min.

1.3 Synthesis of Compounds

(*t*BuCP)₄ (2):

A solution of $(tBuCP)_2$ (0.5 mL, c = 0.6 M in toluene, 0.3 mmol) in THF (3 mL) was irradiated with a UV-lamp ($\lambda = 254$ nm; chromatography lamp) for 3 hours while stirring. Subsequently, the solvent was removed *in vacuo* and the off-white residue was extracted with benzene (5 mL). The solvent was removed, and the white powder was dried *in vacuo* to afford pure (tBuCP)₄ (**2**) without further purification.



 $C_{20}H_{36}P_4$, MW = 400.40 g/mol

Yield: 46 mg (77%)

Analytical data was identical to the previously reported data.³ NMR spectra are given in Figure S6 to Figure S8.

¹**H NMR** (400 MHz, 300 K, C₆D₆) δ = 1.40 (s, 36H, C³H) ppm.

¹³C{¹H} NMR (100 MHz, 300 K, C₆D₆) δ = 31.6 (pseudo-t, J_{PC} = 3.1 Hz, C³), 39.7 (pseudo-t, J_{PC} = 2.4 H, C²), 172.5 (s, C¹) ppm.

³¹**P**{¹**H**} (162 MHz, 300 K, C₆D₆) δ = -23.0 (s) ppm.

3-exo and 3-endo:

A solution of $(tBuCP)_2$ (0.6 mL, c = 2.0 M in toluene, 1 mmol, 1.0 eq.) and *N*-methyl maleimide (1333 mg, 12.0 mmol, 10.0 eq.) in toluene (15 mL) was heated to 70 °C for 5 weeks while stirring. Subsequently, the solvent was removed *in vacuo* and the residual *N*-methyl maleimide was removed by sublimation (oil bath at 50 °C, cooling water *ca*. 25 °C, pressure *ca*. $1 \cdot 10^{-3}$ mbar). The crude product was recrystallized from toluene at -30 °C.



 $C_{15}H_{23}NO_2P_2$, MW = 311.30 g/mol

Yield: 140 mg (37%)

¹**H NMR** (400 MHz, 300 K, C_6D_6) $\delta = 1.07$ (s, 18H, C^4H , C^3H -exo), 1.15 (s, 23H, C^3H -endo), 2.65 (s, 3.5H, C^6H -endo), 2.66 (s, 3H, C^6H -exo), 2.63-2.71 (m, overlapping with C^6H -exo and C^6H -endo, C^4H -endo), 2.75 (s, 2H, C^4H -exo) ppm.

¹³C{¹H} NMR (100 MHz, 300 K, C₆D₆) δ = 24.7 (s, C⁶-exo), 24.8 (s, C⁶-endo), 30.7 (ps t, *J*_{PC} = 9.2 Hz, C⁴-endo), 31.1 (ps t, *J*_{PC} = 5.1 Hz, C³-exo), 31.3 (ps t, *J*_{PC} = 5.0 Hz, C³-endo), 38.5 (ps t, *J*_{PC} = 6.2 Hz, C²-endo), 38.8 (ps t, *J*_{PC} = 6.5 Hz, C²-exo), 42.4 (ps t, *J*_{PC} = 8.2 Hz, C⁴-exo), 167.7 (ps t, *J*_{PC} = 9.3 Hz, C¹-endo), 168.6 (ps t, *J*_{PC} = 8.1 Hz, C¹-exo), 175.2 (ps t, *J*_{PC} = 3.0 Hz, C⁵-endo), 175.9 (ps t, *J*_{PC} = 5.5 Hz, C⁵-exo) ppm.

³¹P{¹H} (162 MHz, 300 K, C₆D₆) $\delta = -85.2$ (s, P-endo), -63.1(s, P-exo) ppm.

³¹**P**(162 MHz, 300 K, C₆D₆) $\delta = -85.2$ (pseudo triplet, ²*J*_{PH} = 13.1 Hz, ³*J*_{PH} = -9.7 Hz, P-endo), -63.1(s, P-exo) ppm.

GC-MS m/z = 311.0 (retention times and additional data given in Figure S1, Figure S2, and Figure S3).



Figure S4. Left: Section of the ³¹P NMR (162 MHz, C₆D₆, 300 K) showing the signal of **3-endo**; experimental (upwards) and simulation (downwards); right: section of the ¹H NMR spectrum of the mixture of **3-exo** and **3-endo** (simulation was not possible due to overlap of signals).

 Table S1. Coupling constants from the iterative fit of the AA'XX' spin system and schematic representation of 3-endo. Only the A part (observed in the ³¹P NMR spectrum) was simulated. The X part observed in the ¹H NMR spectrum was partially obscured due to signal overlap with further ¹H NMR signals.

	$\delta(\mathbf{A}) = -85.23 \text{ ppm}$
х . Н	$\delta(A') = -85.25 \text{ ppm}$
	${}^{1}J_{AA'} = 2.1 \text{ Hz}$
	${}^{2}J_{\rm AX} = 13.1 \; {\rm Hz}$
tBu // Me	${}^{3}J_{A'X} = -9.7 \text{ Hz}$
	${}^{1}J_{\rm XX'} = 0.1 \ {\rm Hz}$

Alternatively, **3-exo** and **3-endo** can be prepared by a photochemical reaction: A solution of $(tBuCP)_2$ (0.3 mL, c = 2.0 M in toluene, 0.6 mmol, 1.0 eq.) and *N*-methyl maleimide (500 mg, 4.5 mmol, 7.5 eq.) in toluene (100 mL) was irradiated with a Hg-lamp for 5 min. Subsequently, the solvent was removed *in vacuo* and the sample was analysed by ³¹P NMR spectroscopy, showing a singlet resonance at -63.1 and a triplet resonance at -85.2 ppm. Subsequently, the solvent was removed *in vacuo* and the residual *N*-methyl maleimide was removed by sublimation (oil bath at 50 °C, cooling water *ca*. 25 °C, pressure *ca*. $1 \cdot 10^{-3}$ mbar). The crude product was recrystallized from toluene at -30 °C.

Single crystals of $(3-exo)_2(3-endo)$ were obtained by slow evaporation from a saturated *n*-hexane solution of a mixture of 3-exo and 3-endo.

Yield: 55 mg (29%)

Analytical data were identical to the data presented above.

1.4 Procedures for other Reactions

NMR scale irradiation of 2

A J. Young valve NMR tube containing a solution of **2** (1.7 mg, 4.3 μ mol) and PPh₃ (5.2 mg, 0.02 mmol) in C₆D₆ (0.5 mL) was placed inside a reaction tube filled with water and irradiated with UV light (365 nm (±15 nm), 24 V, 700 mA) for 15 h using a previously described setup.²

After irradiation for 15 h, the colourless solution containing orange precipitate (Figure S5) was analysed by NMR spectroscopy (NMR spectra depicted in Figure S15 to Figure S17).



Figure S5. Image of the NMR tube after irradiation of 2 to form tBuC=CtBu, small amounts of P4 and orange precipitate.

Reaction of 1 with *N*-phenylmaleimide

A solution of $(tBuCP)_2$ (0.6 mL, c = 1.2 M in toluene, 0.72 mmol, 1.0 eq.) and *N*-phenylmaleimide (173 mg, 2.9 mmol, 4.0 eq.) in THF (200 mL) was irradiated with a Hg-lamp (photoLAB reactor from UV-Consulting Peschl®) for 1 h. Subsequently, the solvent was removed and the yellow residue was dried *in vacuo*. The solid was analysed by ³¹P{¹H} NMR spectroscopy (Figure S18).

Reaction of 1 with maleic anhydride

A solution of $(tBuCP)_2$ (0.2 mL, c = 0.6 M in toluene, 0.1 mmol, 1.0 eq.) and maleic anhydride (59 mg, 0.6 mmol, 5.0 eq.) in THF (200 mL) was irradiated with a UV-lamp ($\lambda = 254$ nm; chromatography lamp) for 2.5 h. Subsequently, the solvent was removed and the residue was dried *in vacuo*. The solid was analysed by ³¹P{¹H} NMR spectroscopy (Figure S19).

Reaction of 1 with bis(trimethylsilyl)acetylene

A J. Young valve NMR tube containing a solution of **1** (0.2 mL, c = 1.2 M in toluene, 0.2 mmol, 1.0 eq.) and bis(trimethylsilyl)acetylene (500 mg, 2.9 mmol, 12.1 eq.) in C₆D₆ (200 mL) was irradiated with a UV-lamp ($\lambda = 254$ nm; chromatography lamp) for 2 h. Subsequently, the reaction mixture was analysed by NMR spectroscopy (Figure S20).

2 NMR Spectra



Figure S6. ¹H NMR spectrum (400 MHz, 300 K, C₆D₆) of 2; *C₆D₆.



Figure S7. ${}^{13}C{}^{1}H$ NMR spectrum (100 MHz, 300 K, C₆D₆) of **2**; *C₆D₆.



Figure S8. ³¹P{¹H} NMR spectrum (162 MHz, 300 K, C₆D₆) of 2.



Figure S9. ³¹P{¹H} NMR spectrum (162 MHz, 300 K, C₆D₆) of **1** upon storage at ambient light with PPh₃ (*) as internal standard.



Figure S10. ${}^{31}P{}^{1}H$ NMR spectrum (162 MHz, 300 K, C₆D₆) of **1** upon storage in the dark with PPh₃ (*) as internal standard.



Figure S11. ¹H NMR spectrum (400 MHz, 300 K, C₆D₆) of a mixture 3-exo and 3-endo; *C₆D₆; °residual toluene.



Figure S12. ¹³C{¹H} NMR spectrum (100 MHz, 300 K, C₆D₆) of a mixture 3-exo and 3-endo; *C₆D₆; °residual toluene.



Figure S13. ${}^{31}P{}^{1}H$ NMR spectrum (162 MHz, 300 K, C₆D₆) of a mixture 3-exo and 3-endo.



Figure S14. ³¹P NMR spectrum (162 MHz, 300 K, C₆D₆) of a mixture 3-exo and 3-endo.



Figure S15. ¹H NMR spectrum (400 MHz, 300 K, C₆D₆) after irradiation of **2** with an LED ($\lambda = 365$ nm). The main signal at 1.23 ppm corresponds to the *t*BuC=C*t*Bu. °PPh₃ (internal standard); *C₆D₆.



Figure S16. ¹³C{¹H} NMR spectrum (100 MHz, 300 K, C₆D₆) after irradiation of **2** with an LED ($\lambda = 365$ nm); all marked signals belong to *t*BuC=C*t*Bu; °PPh₃ (internal standard), *C₆D₆.



Figure S17. ³¹P{¹H} NMR spectrum (162 MHz, 300 K, C₆D₆) after irradiation of **2** with an LED ($\lambda = 365$ nm). The signal at -520.7 ppm corresponds to P₄. *residual **2**; °PPh₃ (internal standard).



Figure S18. ³¹P{¹H} NMR spectrum (162 MHz, 300 K, C₆D₆) of the photoreaction of 1 with *N*-phenylmaleimide.



Figure S19. ³¹P{¹H} NMR spectrum (162 MHz, 300 K, C₆D₆) of the photoreaction of **1** with maleic anhydride. °**1**, ***2**, #possible new photoproducts.



Figure S20. ³¹P{¹H} NMR spectrum (162 MHz, 300 K, C₆D₆) of the photoreaction of 1 with bis(trimethylsilyl)acetylene. $^{\circ}$ 1, *2.



Figure S21. ³¹P{¹H} NMR monitoring of a solution of 1 in toluene showing formation of 2.

3 Single Crystal X-ray Diffraction Data

Single-crystal X-ray diffraction data for $(3\text{-exo})_2(3\text{-endo})(n\text{-hexane})$ was recorded on a XtaLAB Synergy DW R (DW system, HyPix-Arc 150) diffractometer with Cu-K α radiation ($\lambda = 1.54184$ Å). Crystals were selected under mineral oil, mounted on micromount loops and quench-cooled using an Oxford Cryosystems open flow N₂ cooling device. Either semiempirical multi-scan absorption corrections⁴ or analytical ones⁵ were applied to the data. The structure was solved with the SHELXT⁶ solution program using dual methods and by using Olex2 as the graphical interface.⁷ The model was refined with ShelXL⁶ using full matrix least squares minimization on $F^{2.8}$ The hydrogen atoms were located in idealised positions and refined isotropically with a riding model.

A single crystal of **1** was examined on a Rigaku Supernova diffractometer using Mo-K α (λ = 0.71073 Å) radiation. The crystal was kept at 94.0(1) K during data collection. Using Olex2,⁷ the structure was solved with the SHELXT⁶ structure solution program using Intrinsic Phasing and refined with the olex2.refine⁹ refinement package using Levenberg-Marquardt minimisation. The crystal was grown *in situ* in the dark by cooling a 1:1 mixture of the compound with *n*-pentane with 5 K/h to 180 K and subsequently to 94 K with the maximal achievable ramp rate. A twinned crystal was obtained with a ratio of 1:1. The second component was rotated by -169.1° around [0.02 1.00 -0.02] (reciprocal) or [0.06 1.00 -0.02] (direct). Both domains were taken into account for data integration, only the non or minor overlapping reflections of the first domain were used for refinement. All hydrogen atoms were refined isotropically. Details of the X-ray investigation are given in Table S1.

CCDC 2102564 and 2323059 contain the supplementary crystallographic data for this publication. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/conts/retrieving.html.

	1	(3-exo) ₂ (3-endo)
		(<i>n</i> -hexane)
CCDC No.	2102564	2323059
Empirical formula	$C_{10}H_{18}P_2$	$C_{51}H_{83}N_3O_6P_6$
Formula weight / g mol ⁻¹	200.202	1020.02
Temperature / K	94.0(1)	100.0(1)
Crystal system	monoclinic	monoclinic
Space group	P2 ₁	$P2_{1}/c$
<i>a</i> / Å	6.1504(6)	7.79270(10)
b / Å	11.2802(8)	27.0421(3)
<i>c</i> / Å	8.6389(9)	26.5278(2)
α / °	90	90
β/°	98.913(9)	96.2530(10)
y / °	90	90
Volume / Å ³	592.11(10)	5556.97(10)
Ζ	2	4
$ ho_{ m calc}$ /g cm ⁻³	1.123	1.219
μ / mm ⁻¹	0.320	2.178
<i>F</i> (000)	216.4	2192.0
Crystal size / mm ³	0.4 imes 0.25 imes 0.25	$0.286 \times 0.118 \times 0.063$
Radiation	Mo K α ($\lambda = 0.71073$)	Cu K α (λ = 1.54184)
2Θ range for data collection / °	5.98 to 66.4	4.68 to 146.346
	$-9 \le h \le 9,$	$-5 \le h \le 9,$
Index ranges	$-17 \le k \le 17,$	$-32 \le k \le 33,$
	$-13 \le l \le 13$	$-32 \le l \le 32$
Reflections collected	50551	50947
Independent reflections	4538 [$R_{\rm int} = 0.0922$,	10640 [$R_{\rm int} = 0.0214$,
independent reflections	$R_{\rm sigma} = 0.0497$]	$R_{\rm sigma} = 0.0189$]
Reflections with $I \ge 2\sigma(I)$	3600	
Data/restraints/	4538/1/181	10640/0/618
parameters		10010/0/010
Goodness-of-fit on F^2	0.840	1.057
Final R indexes $[I > 2\sigma(I)]$	$R_1 = 0.0270,$	$R_1 = 0.0390, wR_2 =$
	$wR_2 = 0.0541$	0.1015
Final <i>R</i> indexes	$R_1 = 0.0369,$	$R_1 = 0.0431, wR_2 =$
[all data]	$WR_2 = 0.0554$	0.1041
Largest diff. peak/hole / $e A^{-3}$	0.32/-0.19	0.66/-0.43
Flack parameter	0.07(6)	

Table S2. Crystal data and structure refinement for compound 1 and $(3-exo)_2(3-endo)(n-hexane)$.

4 NMR Monitoring Data



Figure S22. Change of concentration of 1 (c₁) over time at 300 K in toluene solution ($c^0 = 0.4 \text{ mol}\cdot\text{L}^{-1}$) as determined by ³¹P NMR spectroscopy in the dark.



Figure S23. Decrease of concentration of 1 upon *in situ* illumination in an NMR tube.

5 Stationary Absorption Spectroscopy with Stepwise Illumination

The steady-state absorption spectra in the UV/Vis were recorded with a referenced single beam photo-spectrometer (Cary 60, Agilent) equipped with a self-build sample compartment allowing for the usage of self-constructed sample cell holders and light emitting diodes (LED) for sample excitation. The photoconversion of **1** in *n*-hexane was followed by recording absorption spectra after stepwise temporally and geometrically defined illumination at λ_{exc} = 340 nm (LED; M340L4, 53 mW, Thorlabs) of the sample in a 10 × 1 mm quartz cell. The temporally rectangular excitation pulses were collimated using an anti-reflection coated aspheric lens (COP-A, Thorlabs) and delivered along the 1 mm path length of the cuvette in an angle of *ca*. 40° to the detection beam. The sample volume was 300 µL so that the entire sample volume was homogeneously illuminated, avoiding possible effects of diffusion during the recording of the spectra.

6 Quantum Chemical Calculations

6.1 Computational Investigation of the Light-induced Planar 1,2-Diphosphacyclubutadiene Formation (Part 1)

Ab initio molecular dynamics simulations (AIMD) were performed starting on the tetrahedrane compound **1** in the gas phase using the AIMD module implemented in Orca.¹⁰The quantum chemical level of theory employed was TD-DFT(B3LYP)//DEF2-TZVP(-F). The Nosé-Hoover chain thermostat (NHC) at 300 K and a time constant of 20 fs was used for a very accurate sampling of the canonical ensemble. The system was propagated in 1 fs steps starting in the ground singlet state for 1 ps and then switched to the excited singlet state. As is evident from the video (diphosphacyclubutadiene_formation.mp4), in the singlet ground state the tetrahedrane form shows at least in the first ps no tendency for any structural conversion. However, once the system is considered to propagate further in the excited singlet domain, the P–P bond immediately elongates from ca. 2.2 Å to ca. 2.9 Å (Figure 7a), the C-C-P angle within the tetrahedral configuration enhances from ca. 65° to ca. 90° (Figure 7b), and the P-C-C-P dihedral angle within the tetrahedral configuration enhances from ca. 80° to ca. 100° (Figure 7c). Then within 2 ps the system flips into the planar 1,2-diphosphacyclobutadiene with a *ca*. 2.1 Å P–P bond, a *ca*. 110° C-C-P angle, and a *ca*. 25° P-C-C-P dihedral angle (Figure S24). When switching back into the singlet ground state potential energy surface after 3 ps of the trajectory, the planar 1,2-diphosphacyclobutadiene configuration maintains stable for at least the next 1 ps. Repeating such sequences of trajectories 6 times always starting from the tetrahedrane configuration, in all cases identical configurational changes are observed (Figure S24). The average along the P–P bond, the C-C-P angle, and the P-C-C-P dihedral angle changes over time of these 6 switching trajectories provides kinetic information of this transformation. A global exponential fit to these averages reveals a lifetime of ca. 960 fs for these structural changes.

For comparison, the isomerisation of **1** to **1'** in the absence of light was calculated on the ω B97X-D3/def2-SVP level of theory using the NEB method and an activation energy of 55.3 kcal·mol⁻¹ was found.



Figure S24. Structural analysis of individual molecular dynamics trajectories showing the P–P bond length (a), the C-C-P angle (b), and the P-C-C-P dihedral angle (c) as defined in d. The colour shaded temporal ranges indicate propagation in different electronic singlet ground state (grey) and the first excited singlet state (red).

6.2 Computational Analysis for Spectral Assignment (Part 2)

Quantum-chemical calculations on all possible dimerization products that potentially contribute to the absorption signals after stepwise illumination, *i.e.*, 2-endo, 2-exo, and 2-twisted (dimerization product between 1 and 1'), were performed using the Firefly QC package,¹¹ which is partially based on the GAMESS (US)¹² source code. All ground state structures were optimised on the level of restricted closed shell density functional theory (RHF-DFT) using the B3LYP functional and the correlation-consistent cc-pVDZ basis set (Figure S25). Complete active space self-consistency field (CASSCF) theory was used to calculate the static correlation energy. 14 contributing π and *n* electrons were included into the CAS, distributed over 12 molecular orbitals (MO), and energy averaging over 15 states with equal weights, *i.e.*, CASSCF(12,12)15, was performed. To calculate the dynamic correlation energy extended multi-configuration quasi-degenerate perturbation theory (XMCQDPT) was used on top of the CASSCF optimised MOs.¹³ In all cases an intruder state avoidance (ISA) denominator shift of 0.02 was used. The polarised continuum model (PCM) was used to account for solvent effects on the electronic transitions with parameters for cyclohexane. The expected electronic transitions of all three compounds are shown in Figure S25.



Figure S25. Calculated electronic transitions of all possible dimerization products in the reaction between two 1' moieties or one 1 with one 1' moiety. a,b: dimerization product 2 in *exo* (black) or *endo* (blue) configuration in gas phase (a) or in cyclohexane (b) as indicated. c,d: a potential dimerization product from a reaction between 1 and 1' in gas phase (c) or in cyclohexane (d) as indicated.

6.3 Computational Analysis for Energetic Considerations in the Dimerization Process (Part 3)

Quantum-mechanical calculations on the dimerization process were performed using the Orca package (version 5.0.4).¹⁴ Two dimensional relaxed scans along the two neighbouring phosphor atoms from each monomer (see Figure 8 for definition) were conducted for each of the three possible dimerization products, *i.e.*, *2-endo*, *2-exo*, and *2-twisted* (dimerization product between 1 and 1'), using restricted closed shell density functional theory (RHF-DFT) with the B3LYP functional and the DEF2-TZVP(-F) basis set with D4 dispersion correction employing the RIJCOSX approximation.

6.4 Electronic Structure and NMR calculations (Part 4)

General Methods

Geometry optimisations and calculations of the frontier molecular orbitals of P₄ and **1** (Figure 4 in the manuscript and were performed with the ORCA program package (versions 4.1 and 4.2).¹⁴ All calculations were conducted in the gas phase. The RI¹⁵ approximation was used for GGA calculations whereas the RIJCOSX approximation was used in hybrid-DFT calculations. Geometry optimisations of **3-endo** and **3-exo** have been carried out at the BP86-D3BJ/def2-TZVP¹⁶ level of theory. NMR calculations of **3-endo** and **3-exo** have been carried out using the TPSS/pcSseg-2¹⁷ level of theory and were referenced to the reported chemical shift of (*t*BuCP)₄.³ Chemcraft¹⁸ and GaussSum¹⁹ were used to visualise the results.



Figure S26. Frontier orbitals of P4 and 1 calculated at the TPSS-D3BJ/def2-TZVP level of theory. Energies are given in eV.

6.5 Calculations of Aromaticity Parameters (Part 5)

The calculations of the magnetically induced current density in the molecules were performed by obtaining the density matrices and the magnetically perturbed density matrices with the TURBOMOLE²⁰ program using the hybrid B3LYP²¹ density functional and the triple- ζ def2-TZVP¹³ basis set. The m5 quadrature grid²² was employed as well as the resolution-of-identity (RI) approximation.²³ These data are used as input for the gauge-including magnetically induced current (GIMIC) program at the limit of a vanishing magnetic field.²⁴ Gauge-including atomic orbital (GIAO), or London orbitals, are employed to ensure gauge-origin independence.²⁵

The magnetically induced current density was investigated visually in the Paraview²⁶ program using streamlines. The strength of the current density was obtained by placing integration plane that cross the current-density flux as illustrated in Figure 5. The magnetic flux density, $B = (0,0, -B_z)$, is parallel to one of the dimensions of the integration plane, which we call vertical. The planes extend far above and below the molecule until the current density vanishes. Likewise, in the horizontal direction, the integration planes cover the distance from the geometrical centre of the tetrahedron formed by the core of the clusters out towards infinity. The dimensions of the employed integration planes are $8 \times 16 a_0$ for P₄, $10 \times 18 a_0$ for **1**, and $10 \times 22 a_0$ for $(tBuC)_4$ (atomic units are employed where $1 a_0 = 0.529$ Å). The integration planes were split vertically in slices $0.02 a_0$ wide, which allowed us to plot the differential current profile, dJ^B/dr , and identify the current-density domains.

Cartesian Coordinates for Optimised Structures

1:

Р	-5.12137783907350	0.39967169899593	0.28610730456242
С	-3.36123120451169	-0.12777555265565	0.51961291438714
С	-3.52096836044728	0.90274670987689	-0.49937014088859
Р	-3.51492315387866	1.57802271846826	1.22541110778401
С	-2.63937305697805	-1.39840157122337	0.87945358653299
С	-3.06896509627181	1.36866978257099	-1.85722489925801
С	-1.55467122620358	1.64533729916710	-1.83409127302251
С	-3.82459943934436	2.66582564439220	-2.19279439363964
С	-3.39573008025164	0.29439066822668	-2.91045603237571
С	-2.96815054867160	-2.49260499465574	-0.15250610247847
С	-3.11953344476288	-1.84223309442971	2.27176455062166
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Η	-2.45521583813124	-3.42434596003219	0.11058060053172

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С	1.96617666844349	2.20454652362447	2.54244803831732
С	0.30200526093422	4.41562497972131	4.84912832867238
Η	1.09633234335402	4.68921639664403	4.14569696073796
Η	0.74617092680789	3.80002051898595	5.64657940544927
Η	-0.06369612948686	5.34791662783851	5.30910651320313
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Η	-1.57743877948766	2.81928070217586	6.07031756394356

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С	-1.47052748354283	4.52284145700997	3.03120829820179
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С	-0.72230338565779	2.33969170946494	3.33993130232594
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С	0.11497532921615	4.16197539452448	4.93531104561292
Η	1.05785613737047	4.36830460446381	4.39581217025910
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Ν	5.27275266263484	15.09001412082902	7.59153124213867
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Η	6.49863714802505	15.95938493587400	6.11358981921093
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Η	0.36188387769407	15.92949646768986	13.92040585330996
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Ν	4.95743907379257	6.13740381808845	5.01818814587821
С	5.75464386566494	5.03066753042808	5.34488554002593
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С	4.15410732326557	4.52772540937203	8.65246547397892
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С	4.56530187477724	9.44720073771016	8.17714780692995
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С	4.87713461396563	3.16555265855926	8.65103616179971
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С	3.51427463130877	4.71417933817291	10.04272637457767
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Η	3.49794649459348	4.15094528468882	6.60270040300480
Η	7.67823951891610	7.62660715801389	5.53765671274036

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