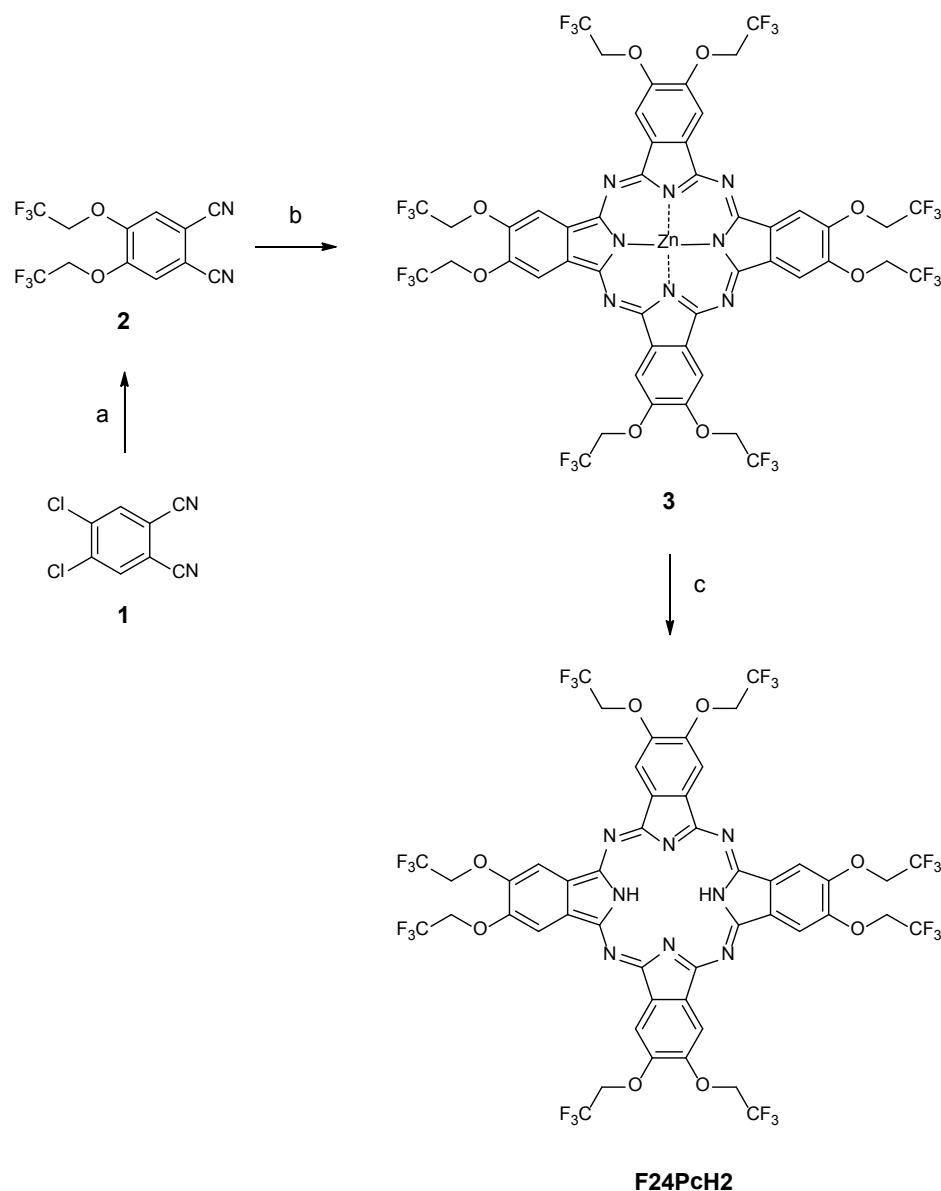


Real-time single-molecule imaging of quantum interference

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1) Synthesis of F24PcH2

The synthesis of **F24PcH2** is displayed in figure S1. Synthetic protocols and analytical data of the target structure and the precursors are provided.



Supplementary Figure S1 | Synthesis of F24PcH2. Reagents and conditions: (a) HOCH_2CF_3 , K_2CO_3 , DMSO, MW, 100°C , 1 h, 88%; (b) DBU, $\text{Zn}(\text{OAc})_2$, pentanol, MW, 170°C , 12 h, 78%; (c) pyridine-HCl, pyridine, 120°C , 18 h, 76%.

General Remarks

All commercially available starting materials were of reagent grade and used as received. Dry dimethyl sulfoxide (DMSO) and dry pyridine were purchased from *Fluka*, stored over 4 Å molecular sieves, and handled under argon. The solvents for chromatography and extraction were of technical grade and distilled prior to use. Column chromatography purifications were carried out on *silica gel 60* (particle size 0.040–0.063 mm) from *Fluka*. Deuterated solvents were purchased from *Cambridge Isotope Laboratories*. ^1H , ^{19}F and ^{13}C NMR spectra were recorded with a *Bruker DMX 400* instrument (^1H resonance 400 MHz) at 298 K. UV/Vis spectra were recorded on a *UV-1800* spectrophotometer from *Shimadzu*. Matrix Assisted Laser Desorption Ionisation Time of Flight (MALDI-ToF) mass spectra were performed on an *Applied Bio Systems Voyager-De™ Pro* mass spectrometer. Electron-impact quadrupole mass spectra were recorded on a *GCMS-QP2010 SE* from *Shimadzu*. Elemental analyses were performed on a *Perkin-Elmer Analysator 240*. Microwave reactions were carried out with an *Initiator 8* (400 W) from *Biotage*.

4,5-Bis(2,2,2-trifluoroethoxy)phthalonitrile (2): 4,5-Dichlorophthalonitrile (**1**, 200 mg, 1.02 mmol, 1.0 eq.), 2,2,2-trifluoroethanol (609 mg, 6.09 mmol, 6.0 eq.) and potassium carbonate (842 mg, 6.09 mmol, 6.0 eq.) were added to dry DMSO (10 mL) in a microwave vial (*Biotage* microwave vial 10–20 mL). The sealed tube was heated in a microwave apparatus to 100 °C for one hour. After cooling to room temperature water was added to the reaction mixture. The mixture was extracted with dichloromethane. The combined organic phases were washed with brine and subsequently dried over magnesium sulfate. After evaporation of the solvent under reduced pressure the crude was purified by column chromatography (silica gel; cyclohexane/ethyl acetate, 4:1) to afford 4,5-bis(2,2,2-trifluoroethoxy)phthalonitrile (291 mg) as a white solid in a yield of 88%.

^1H NMR (400 MHz, CDCl_3): δ 7.33 (s, 2H), 4.51 (q, J = 7.7 Hz, 4H); ^{19}F NMR (376 MHz, CDCl_3): δ -73.7 (t, J = 7.7 Hz, 6F); ^{13}C NMR (101 MHz, CDCl_3): δ 151.0, 122.6 (q, J = 278 Hz), 120.2, 114.7, 111.6, 67.4 (q, J = 37 Hz). MS (EI-QMS, m/z): 324 (100%, M^+), 241 (25%), 171 (35%), 83 (45%).

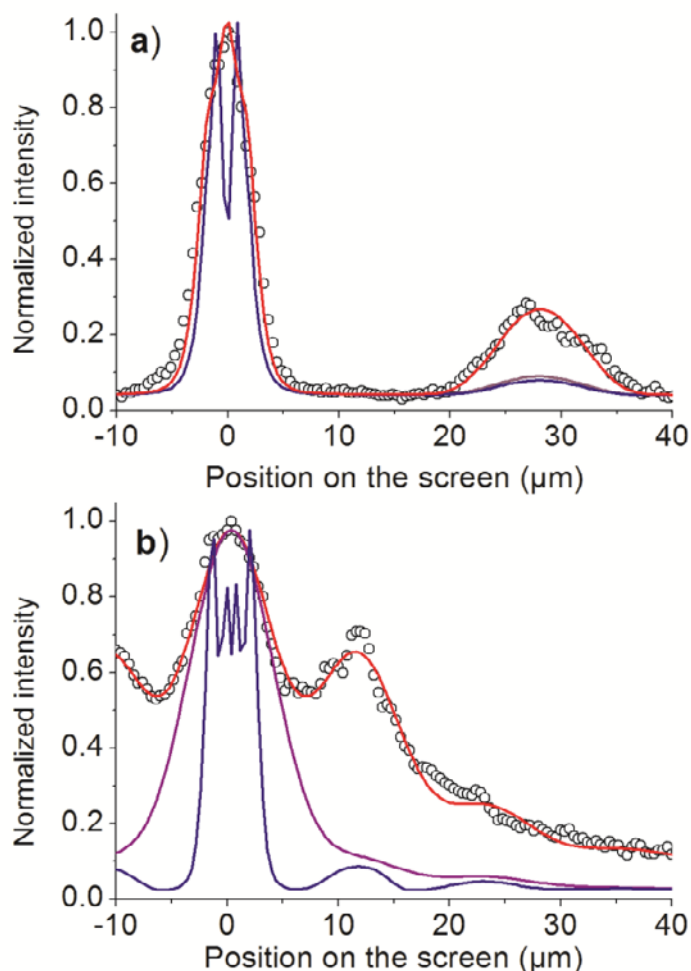
2,3,9,10,16,17,23,24-Octakis(2,2,2-trifluoroethoxy)phthalocyaninatozinc(II) (3): 4,5-Bis(2,2,2-trifluoroethoxy)phthalonitrile (**2**, 100 mg, 308 μmol , 1.0 eq.), zinc acetate (14.2 mg, 77.1 μmol , 0.25 eq.) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 46 μL , 47 mg, 308 μmol , 1.0 eq.) were added to pentanol (3.5 mL) in a microwave vial (*Biotage* microwave vial 2–5 mL). The sealed tube was heated in a microwave apparatus to 170 °C for 12 hours. After cooling to room temperature the solvent was removed by distillation at ambient pressure. Diethylether was added and the solution was washed successively with water and brine. The organic phase was dried over magnesium sulfate. After evaporation of the solvent under reduced pressure, the crude was purified by column

chromatography (silica gel; diethylether/hexane 8:2 then 9:1) to afford 2,3,9,10,16,17,23,24-octakis(2,2,2-trifluoroethoxy)phthalocyaninatozinc(II) (82 mg) as a blue solid in a yield of 78%.

^1H NMR (400 MHz, d_6 -acetone): δ = 8.50 (s, br, 8H), 5.30 (m, 16H); $^{19}\text{F}\{\text{H}\}$ NMR (376 MHz, d_6 -acetone): δ -74.3 (s, 24F); MS (MALDI-ToF, m/z): 1360 (100%, M^+); UV/Vis (acetone): λ_{max} = 360, 600, 635, 664 nm.

2,3,9,10,16,17,23,24-Octakis(2,2,2-trifluoroethoxy)phthalocyanine (F24PcH2): 2,3,9,10,16,17,23,24-Octakis(2,2,2-trifluoroethoxy)phthalocyaninatozinc(II) (**3**, 70 mg, 51.4 μmol , 1.0 eq.) and pyridine hydrochloride (1.50 g) were added to dry pyridine (3 mL). The mixture was stirred under argon at 120 °C for 18 hours. Water (15 mL) was added to the hot reaction mixture. After cooling to room temperature the resulting precipitate was collected by centrifugation. The dark blue precipitate was washed successively with H_2O , methanol, acetone and diethylether, and subsequently dried under high vacuum to yield **F24PcH2** (51 mg) as a blue solid in a yield of 76%. The metal-free phthalocyanine **F24PcH2** is completely insoluble in common organic solvents and was thus exclusively characterized by solid-state analytical methods like MALDI-ToF mass spectrometry and elemental analysis.

MS (MALDI-ToF, m/z): 1298 (100%, M^+); Elemental analysis (calcd., found for $\text{C}_{48}\text{H}_{26}\text{F}_{24}\text{N}_8\text{O}_8$): C (44.39, 44.42), N (8.63, 8.77), H (2.02, 2.16).

2) Numerical modeling of the diffraction images:**Supplementary Figure S2 | Significance of the van der Waals force**

A numerically correct fit of the experimental data (hollow circles) requires first and foremost the assumption that even complex molecules such as PcH2 (a) and F24PcH2 (b) propagate as delocalized quantum waves. Only this assumption produces diffraction side peaks with the correct separation (blue bottom curves in (a) and (b)) and also the correct dependence on the molecular velocity. If molecules were perfectly coherent plane waves one would also expect to see some remnants of near-field diffraction in the central lobe up to $\pm 5 \mu\text{m}$. In practice, this is not visible since the final interferogram is further modulated by the following effects. On the one hand the source has a finite width and finite transverse coherence. For PcH2 (a) this effect eliminates already all oscillations in the central lobe, but it does not alter significantly the height of the higher interference fringes (purple curve right on top of the blue curve). For F24PcH2 (b) the source coherence adds only a minor broadening to the more dominant smearing of the diffraction pattern by $3 \mu\text{m}$ which is compatible with the assumption of increased surface diffusion. All numerical curves represent an incoherent sum of coherent interferograms that were computed for different velocities (de Broglie

wavelengths), weighted by the experimentally measured velocity distribution.

Finally, we have to include the van der Waals attraction which tends to deflect the molecules towards the grating bars. The visual effect on the screen is similar to the effect of a narrowing of the grating slits by almost a factor of two. Correspondingly the height of the side-lobes is dramatically increased over a pattern in the absence of dispersion forces (red continuous line with near-perfect fit to the data).

3) Supplementary Table T1: Equipment and settings of the imaging optics for all experiments:

Camera	Andor iXon EMCCD DV8285_BV	Pixel read-out	13 MHz
CCD Temp.	-85°C	Pre-amp. Gain	4.1
Software	Andor Solis vs. 4.11.30001.0	Filters	1x DCXR680, 2x HC711/25 slightly rotated to block Raman scattering
Tube lens	Zeiss, f=164mm		
Objectives	Zeiss Plan Neofluar	Image bit depth	14

Figure No.	2	3a-3d	3e	4a	4b
Illumin. time	24 s	3 s	10 s	1 s	1 s
Illumin. intens.	28 W/cm ²	23 W/cm ²	23 W/cm ²	6 W/cm ²	6 W/cm ²
Pixel size	(0.2 μm) ²	(0.2 μm) ²	(0.4 μm) ²	(0.4 μm) ²	(0.4 μm) ²
Magnification	40x, NA=0.9	40x, NA=0.9	20x, NA=0.5	20x, NA=0.6	20x, NA=0.7
EM Gain	110	150	150	150	150
Colorbar		LUT "hot" linear	LUT "hot" linear	LUT "hot" linear	LUT "fresh" linear
Colorbar max.		120	650	400	600
Colorbar min.		-5	-30	-20	-20
# of pixels with values > max	0	0/3/11/132	0	17	11
# of pixels with values < min	0	0/0/0/0	27	52	28
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