Supporting Information

Luminogens for Aggregation-Induced Emission via Titanium-Mediated Double Nucleophilic Addition to 2,5-Dialkynylpyridines: Formation and Transformation of the Emitting Aggregates

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1. Synthetic procedures and characterization of 2,6-bis(arylethynyl)pyridines:

**General Procedure 2 (GP-2)**

![Chemical structure](image1)

To a stirring mixture of 2,6-dibromopyridine (1.0 equiv), CuI (0.080 equiv), triphenylphosphine (0.080 equiv) and PdCl₂(PPh₃)₂ (0.040 equiv) in degassed triethylamine (2 mL each millimole of 2,6-dibromopyridine), an arylacetylene (2.2 equiv) was added dropwise. The mixture was stirred at rt or under reflux for 2–5 days depending on the target compound (see the following analytics), then filtered at rt. The filtrate was adsorbed over celite and purified by column chromatography (SiO₂, eluent gradient: petroleum ether:ethylacetate = 50:1 to 4:1, 0.5 vol% NEt₃), thus yielding the corresponding 2,6-bis(arylethynyl)pyridine as pale yellow solid (28–80%).

**2,6-bis((4-fluoro-3-methylphenyl)ethynyl)pyridine**, pale yellow solid, 1.2 g, 3.5 mmol, Yield: 56%. 2,6-dibromopyridine (1.5 g, 6.3 mmol); 4-ethynyl-1-fluoro-2-methylbenzene (1.9 g, 1.9 mL); CuI (0.10 g); PPh₃ (0.13 g); PdCl₂(PPh₃)₂ (0.18 g); NEt₃ (13 mL). Room temperature, 5 days. 

$^1$H NMR (600.13 MHz; C₆D₆; 295.0 K): $\delta$ [ppm] = 7.21 – 7.16 (m, 3 H), 7.15 – 7.12 (m, 2 H), 7.08 (d, $J = 7.8$ Hz, 2 H), 6.81 (t, $J = 7.8$ Hz, 1 H), 6.64 – 6.54 (m, 2 H), 1.86 (d, $J = 1.9$ Hz, 6 H). $^{13}$C($^1$H) NMR (150.90 MHz; C₆D₆; 295.0 K): $\delta$ [ppm] = 162.0 (d, $J = 248.9$ Hz), 144.6, 136.1, 135.8 (d, $J = 5.6$ Hz), 131.7 (d, $J = 8.5$ Hz), 125.9, 125.7 (d, $J = 18.1$ Hz), 118.5 (d, $J = 3.8$ Hz), 115.6 (d, $J = 23.3$ Hz), 89.0 – 88.9 (m), 14.1 (d, $J = 3.4$ Hz). MS (HR-El(+)): calcd 344.1251 (C₂₃H₁₇F₂N, [M+H]+), found 344.1251.
**2,6-bis((3-fluorophenyl)ethynyl)pyridine**, pale yellow solid, 4.4 g, 14 mmol, Yield: 80%. 2,6-dibromopyridine: (2.6 g, 11 mmol); 1-ethynyl-3-fluorobenzene (2.9 g, 2.8 mL); Cul (0.17 g); PPh₃ (0.23 g); PdCl₂(PPh₃)₂ (0.31 g); NEt₃ (22 mL). Room temperature, 4 days. ¹H NMR (399.89 MHz; C₆D₆; 295.0 K): δ [ppm] = 7.25 – 7.13 (m, 4 H), 7.04 (d, J= 7.8 Hz, 2 H), 6.86 – 6.79 (m, 1 H), 6.77 – 6.61 (m, 4 H). ¹³C{¹H} NMR (100.55 MHz; C₆D₆; 296.4 K): δ [ppm] = 162.7 (d, J= 246.7 Hz), 144.1, 136.1, 130.3 (d, J= 8.2 Hz), 128.1 (d, J= 3.1 Hz), 126.3, 124.5 (d, J= 9.5 Hz), 119.0 (d, J= 23.0 Hz), 116.5 (d, J= 21.1 Hz), 90.1, 88.2 (d, J= 3.4 Hz). MS (HR-EI(+)): calcd 316.0938 (C₂₁H₁₃F₂N, [M+H]+), found 316.0929.
2,6-bis((3,5-difluorophenyl)ethynyl)pyridine, pale yellow solid, 1.3 g, 3.7 mmol, Yield: 60%. 2,6-dibromopyridine: (1.4 g, 6.0 mmol); 1-ethyl-3,5-difluorobenzene (1.8 g, 1.6 mL); Cul (0.091 g); PPh₃ (0.13 g); PdCl₂(PPh₃)₂ (0.17 g); NEt₃ (12 mL). Room temperature, 5 days. ¹H NMR (399.89 MHz; C₆D₆; 295.4 K): δ [ppm] = 6.98 (d, J= 7.8 Hz, 2 H), 6.91 – 6.64 (m, 5 H), 6.49 – 6.12 (m, 2 H). ¹³C(¹H) NMR (100.55 MHz; C₆D₆; 296.2 K): δ [ppm] = 163.1 (d, J= 249.2 Hz), 162.9 (d, J= 249.5 Hz), 143.8, 136.3, 126.7, 125.3 – 125.0 (m), 115.2 (d, J= 19.3 Hz), 115.1 (d, J= 19.3 Hz), 105.6 – 105.1 (m), 90.7, 87.2 – 87.1 (m). MS (HR-EI(+)): calcd 352.0749 (C₂₁H₁₁F₄N, [M+H]+), found 352.0745.
2,6-bis((4-(tert-butyl)phenyl)ethynyl)pyridine. pale yellow solid, 1.2 g, 3.0 mmol, Yield: 28%. 2,6-dibromopyridine: (2.6 g, 11 mmol); 1-(tert-butyl)-4-ethynylbenzene (3.8 g, 4.3 mL); CuI (0.17 g); PPh₃ (0.23 g); PdCl₂(PPh₃)₂ (0.31 g); NEt₃ (22 mL). Reflux, 2 days. ¹H NMR (600.13 MHz; C₆D₆; 295.0 K): δ[ppm] = 7.61 – 7.53 (m, 4 H), 7.13 – 7.17 (m, 4 H), 7.05 (d, J= 7.8 Hz, 2 H), 6.74 (t, J= 7.8 Hz, 1 H), 1.09 (s, 18 H). ¹³C{¹H} NMR (150.90 MHz; C₆D₆; 295.0 K): δ[ppm] = 152.3, 144.7, 136.0, 132.3, 125.88, 125.85, 120.0, 89.9, 89.3, 34.7, 31.1. MS (HR-EI(+)): calcd 392.2378 (C₂₉H₃₁N, [M+H]⁺), found 392.2371.
2. $^1$H NMR and $^{13}$C($^1$H) NMR Spectra of 2,6-bis(1,2,2-triarylvinyl)pyridines

Compound 1
Compound 2
Compound 3
Compound 4
Compound 6
3. Additional information on Compound 2.

Figure S1. $^{19}$F($^1$H) NMR spectrum of 4 in C$_6$D$_6$. Splitting of singlets suggests the presence of two rotamers of 4 in solution.

Figure S2. Top: π-π stacking in the X-ray diffraction structure of 2. Torsion: 79.30°, Cg-Cg' distance: 3.868 Å. Bottom: X-ray diffraction molecular structure of 2.
4. Extinction, absorption and fluorescence emission spectra, DLS experiments

Supporting data for compound 1

Figure S3. Photoluminescence excitation/emission (PLE) maps of 1 for different water/acetonitrile mixtures. A) 1 in 50% v/v H$_2$O measured right after mixing and B) after 24h. C) 1 in 70% v/v H$_2$O measured right after mixing and D) after 24h. E) 1 in 90% v/v H$_2$O measured right after mixing and F) after 24h. The dispersions were kept at rest in quartz cuvettes under light exclusion until the measurements were completed.
Figure S4. Evolution of extinction, PL emission and excitation spectra of 1 over time for different water/acetonitrile mixtures. A-C) Extinction spectra of 1 in 50, 70 and 90% v/v H₂O, respectively, measured over time. D-F) PL emission of 1 in 50, 70 and 90% v/v H₂O, respectively, measured over time (λₑₓ = 330 nm). G-I) PL excitation spectra of 1 in 50, 70 and 90% v/v H₂O, respectively, measured over time (λₑᵢₐₓ = 475 nm). No significant changes of the spectra for the 50% v/v H₂O mixture are observed over time, which is consistent with negligible aggregation. For the 70% v/v H₂O mixture, all the spectra change drastically due to aggregation. After 72h most of the material has sedimented, as suggested by a dramatic drop in the extinction and PL intensity. The 90% v/v H₂O mixture shows minor changes over time. The extinction spectra show a slight scattering background. PL emission and excitation show minor changes over time after an initial increase during the first 24h. The dispersions were kept at rest inside quartz cuvettes under light exclusion until the measurements were completed.
Figure S5. Scattering background in the non-resonant regime of the extinction spectra of 1 over time for different water/acetonitrile mixtures. The linear trend in the non-resonant regime on a double logarithmic scale allows to extract the scattering exponent \( \cdot m \) from the slope of a line fit (see supplementary section 6 for further explanation). A-C) Non-resonant scattering contribution and linear fits of 50\% (A), 70\% (B) and 90\% (C) v/v H\(_2\)O, respectively. The dispersions were kept at rest in quartz cuvettes under light exclusion until the measurements were completed.

Figure S6. Dynamic light scattering (DLS) experiments of 1 over time. The evolution of the spectra over time is shown for the 50\% (A), 70\% (B) and 90\% (C) v/v H\(_2\)O mixtures. Color key for the time evolution: green (\( t_0 \)) to red (\( t=4 \) days). Data are not significant for the 50\% v/v H\(_2\)O mixture due to insufficient signal-to-noise ratio (A). In the 70\% v/v H\(_2\)O mixture particles grow over the time approaching an average particle size as big as 530 nm; precipitation then occurs, leaving in suspension only a minor fraction of smaller particles (160 nm ca., red curves). In the 90\% v/v H\(_2\)O mixture the average particle size grows moderately from 130 nm to 160 nm over time resulting in an overall stable colloid. The dispersions were kept at rest inside quartz cuvettes under light exclusion until the measurements were completed.
Figure S7. Photographic representation of the viscochromic response of 1 (150µM) in DMSO/glycerol mixtures upon increasing the fraction of glycerol under UV illumination (λexc = 360 nm). The viscosity of the mixture, and therefore the PL intensity, increase with increasing amount of glycerol added due to aggregation-independent RIM. Top left: DMSO solution of 1; Bottom right: 1 after addition of glycerol to the final ratio DMSO/glycerol = 1:8 mixture.

Spectral data compounds 1-5

Figure S8. Five different luminogens under investigation. A-E) Photoluminescence (PL) spectra of 1–5 (from left to right) in different water/acetonitrile mixtures. F-J) Extinction spectra of 1–5 in the same solvent mixtures described for the PL spectra.
Figure S9. Absorbance spectra of 1–4. True absorbance spectra, which were measured with the aid of an integrating sphere, show negligible optical density for 1–4 in the non-resonant regime (λ>400nm) for all the solvent mixtures under investigation. As discussed in the main text, the scattering background can be determined as the difference between the extinction spectra (Figures S4, S10–14) and the absorbance spectra shown in this Figure.
**PL and Extinction Evolution of 1**

![Plots showing intensity and extinction evolution of Compound 1 over time](image)

**Figure S10. Behaviour of Compound 1 over time.** A-E) Photoluminescence spectra and F-J) extinction spectra of 1 for different acetonitrile/water mixtures, measured right after mixing and then after 24 h and 48 h. (A, F) and 90% (B, G) v/v H$_2$O are relatively stable over 48h, in terms of both emission and extinction, with exception of a moderate increase of the emission intensity over time for the 95% v/v H$_2$O mixture. The 80% v/v H$_2$O mixture shows minor changes in the emission spectra (C) but a substantial increase of scattering intensity, along with a pronounced red shift, in the extinction spectra (H). The evolution of the extinction profiles is even more pronounced in the 70% v/v H$_2$O mixture (I), where a strong increase in the scattering intensity can be observed after 24 h but then a dramatic drop in the overall extinction occurs. Moreover, a pronounced blue shift in the emission (D) can be observed over time in this mixture. A faint emission, which drops further in intensity over time (E), is accompanied by a drop of optical extinction over time for the 60% v/v (H$_2$O) mixture (J). Notably, the scattering background in the non-resonant regime is in this case negligible.
e S11. Behaviour of Compound 2 over time A-E) Photoluminescence spectra and F-J) extinction spectra of 2 for different acetonitrile/water mixtures, measured right after mixing and then after 24 h and 48 h. The 95% v/v H$_2$O mixture (A, F) is the most stable over time. The 90% v/v H$_2$O mixture (B, G) shows increasing emission intensity and increasing scattering intensity over time. The 80% v/v H$_2$O mixture (C, H) shows major changes in the emission spectra (C), including a blue shift and a drop in the emission intensity, as well as in the extinction spectra (H), where the scattering contribution rises significantly over time. Similar features can be found in the spectra of 2 in 70% v/v H$_2$O mixtures (D, I), with exception of the absence of blue shifts in the emission. A faint emission, which drops further in intensity over time (E), is accompanied by a drop of optical extinction over time for the 60% v/v H$_2$O mixture (J).
Figure S12. Behaviour of Compound 3 over time. A-E) Photoluminescence spectra and F-J) extinction spectra of 3 for different acetonitrile/water mixtures, measured right after mixing and then after 24 h and 48 h. Mixtures with 95% (A, F) and 90% (B, G) v/v H$_2$O are relatively stable over 48h, in terms of both emission and extinction, with exception of a moderate increase of the emission intensity over time for the 95% v/v H$_2$O mixture (A) and of the scattering intensity in the non-resonant regime for the 90% v/v H$_2$O mixture (G). The 80% v/v H$_2$O mixture shows minor changes in the emission spectra (C) but a substantial increase of scattering intensity over time in the extinction spectra (H). The 70% v/v H$_2$O mixture (D, I) shows major changes in the emission spectra (D), involving a strong blue shift, as well as in the extinction spectra (I), where the scattering contribution rises significantly after 24 h. Differently from what observed for the previous compounds, PL intensity of the 60% v/v (H$_2$O) mixture is not negligible and does not drop significantly over time (E). Notably, the scattering background in the non-resonant regime is remarkable in the freshly prepared 60% v/v H$_2$O mixture and drops over time (J).
Figure S13. Behaviour of Compound 4 over time. A-E) Photoluminescence spectra and F-J) extinction spectra of 4 for different acetonitrile/water mixtures, measured right after mixing and then after 24 h and 48 h. The 95% v/v H₂O mixture (A, F) is relatively stable over time, while the PL and scattering intensity grow over time for the 90% v/v H₂O mixture (B, G). The 80% v/v H₂O mixture shows minor changes in the emission spectra (C) but a substantial increase of scattering intensity and red shift over time in the extinction spectra (H). The 70% v/v H₂O mixture (D, I) shows major changes in the emission spectra (D), involving a strong blue shift over time, as well as in the extinction spectra (I), where the scattering intensity rises after 24 h and then drops significantly. A drop in the PL (E) and extinction (J) intensities can be observed over time for the 60% v/v H₂O mixture.

Figure S14. Behaviour of Compound 5 over time. A-E) Photoluminescence spectra and F-J) extinction spectra of 5 for different acetonitrile/water mixtures, measured right after mixing and then after 24 h and 48 h. Mixtures with 95% (A, F) and 90% (B, G) v/v H₂O are relatively stable over 48h, in terms of both emission and extinction, with exception of a moderate increase of scattering intensity over time for the 90% v/v H₂O mixture (G). The 80% v/v H₂O mixture shows minor changes in the emission spectra (C) but a substantial increase of scattering intensity, along with a pronounced red shift, in the extinction spectra (H). The evolution of the extinction profile is even more pronounced in the 70% v/v H₂O mixture (I), where a strong
increase in the scattering intensity can be observed after 24 h but then a dramatic drop in the overall extinction occurs. A faint emission (E) and negligible scattering intensity (J) can be observed for the 60% v/v H$_2$O mixture.

Figure S15. Emission spectra of 1–6 as spin-coated solid films ($\lambda_{exc} = 330$ nm).
5. X-ray crystal structure determinations

Crystal data and details of the structure determinations are compiled in Table S1. Full shells of intensity data were collected at low temperature with a Bruker AXS Smart 1000 CCD diffractometer (Mo-Kα radiation, sealed X-ray tube, graphite monochromator, compound 4-C₆D₆) or an Agilent Technologies Supernova-E CCD diffractometer (Mo- or Cu-Kα radiation, microfocus X-ray tube, multilayer mirror optics, all other compounds). Detector frames (typically ω-, occasionally ϕ-scans, scan width 0.4...1°) were integrated by profile fitting. Data were corrected for air and detector absorption, Lorentz and polarization effects and scaled essentially by application of appropriate spherical harmonic functions. Absorption by the crystal was treated with a semiempirical multiscan method (as part of the scaling process), and augmented by a spherical correction or numerically (Gaussian grid). For datasets collected with the microfocus tubes an illumination correction was performed as part of the numerical absorption correction.

The structures were solved by ab initio dual space methods (compound 3-n-pentane: SHELXD, compound 4-C₆D₆ pentane: VLD procedure) or by the charge flip procedure and refined by full-matrix least squares methods based on F² against all unique reflections. All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms were input at calculated positions and refined with a riding model. Split atom models were used to refine disordered groups and/or solvent molecules. When found necessary, suitable geometry and adp restraints were applied. Due to severe disorder and fractional occupancy, electron density attributed to solvent of crystallization was removed from the structures of 3 (n-pentane) and 5 (ethyl acetate) with the BYPASS procedure as implemented in PLATON (squeeze/hybrid). Partial structure factors from the solvent masks were included in the refinement as separate contributions to Fcalc.

To establish comparability with the other structures, the previously published structure of 1 was re-refined with hydrogen atoms at calculated positions (refined riding).

CCDC 1965537 and 1963833 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre's and FIZ Karlsruhe's joint Access Service via https://www.ccdc.cam.ac.uk/structures?.
**Table S1.** Details of the crystal structure determinations of compounds 1, 3–5.

|                  | 1             | 3-n-pentane   | 4-C₆D₆    | 5-ethyl acetate |
|------------------|---------------|---------------|-----------|----------------|
| formula          | C₄₅H₂₇F₆N    | C₅₆H₃₁F₆N   | C₅₁H₂₁D₁₇F₆N | C₄₉H₃₆F₁₂NO |
| crystal system   | monoclinic    | orthorhombic  | orthorhombic | orthorhombic   |
| space group      | P 2ᵢ/n       | P 2₁2₁2₁    | P 2₁2₁2₁  | F ddd          |
| a /Å             | 16.1155(4)    | 9.5306(4)    | 9.452(5)  | 22.7164(4)     |
| b /Å             | 10.2929(3)    | 21.4845(7)   | 19.596(10)| 22.8797(4)     |
| c /Å             | 20.6155(5)    | 22.4767(8)   | 21.407(10)| 31.3763(6)     |
| V /Å³            | 3419.27(14)   | 4602.3(3)    | 3965(3)   | 16307.7(5)     |
| Z                | 4             | 4             | 4         | 16             |
| Mᵣ              | 695.67        | 851.97       | 779.82    | 875.73         |
| F₀₀₀             | 1432          | 1792         | 1600      | 7136           |
| d₀ /Mg·m⁻³       | 1.351         | 1.230        | 1.306     | 1.427          |
| μ /mm⁻¹          | 0.101         | 0.715        | 0.094     | 0.123          |
| max., min.       | 1.000, 0.804  | 1.000, 0.806 | 0.862, 0.827 | 1.000, 0.733  |
| transmission     | X-radiation, λ /Å |            |           |                |
| Mo-Ka, 0.71073   | Cu-Ka, 1.54184 | Mo-Ka,       | Mo-Ka,     |                |
| data collect. temperat. /K | 120(1) | 120(1) | 100(1) | 120(1) |
| θ range /°       | 2.2 to 30.6   | 2.8 to 67.3  | 2.2 to 30.6 | 2.2 to 32.6  |
| index ranges h, k, l | ±23, ±14, ±29 | ±11, ±25, ±26 | ±13, ±27, ±30 | ±34, ±34, ±47 |
| reflections       | 73029         | 125836       | 98434     | 88584          |
| measured         | unique [R_int] | 10459 [0.0795]| 8247 [0.2048]| 12146 [0.0687]| 7458 [0.0838]|
| observed [I≥2σ(I)] | 6833   | 4834         | 8267      | 4780           |
| data / restraints /parameters | 10459 / 0 / 469 | 8247 / 160 / 595 | 12146 / 19 / 573 | 7458 / 0 / 263 |
| GooF on F²       | 1.030        | 0.958        | 1.015     | 1.048          |
| R indices [F>4σ(F)] R(F), wR(F²) | 0.0575, 0.1130 | 0.0550, 0.1147 | 0.0583, 0.1389 | 0.0544, 0.1301 |
| R indices (all data) R(F), wR(F²) | 0.0969, 0.1293 | 0.1145, 0.1409 | 0.1000, 0.1623 | 0.0909, 0.1458 |
| absolute structure parameter |                | 0.10(11) | -0.3(2) |                |
| largest residual peaks /e·Å⁻³ | 0.346, -0.245 | 0.169, -0.180 | 0.416, -0.350 | 0.317, -0.224 |
| CCDC deposition number | 1965537 | 1963833    | 1963834   | 1963835        |

* Semi-empirical absorption correction; b numerical absorption correction; c standard uncertainties include systematic error contributions from Monte Carlo simulations.

Deposition numbers for 1: 1817691 (old) and 1965537 (present), 2-n-pentane: 1817692.516
6. Wavelength-dependent scattering

While light scattering is typically investigated as function of scattering angle,\textsuperscript{S17} its wavelength dependence is much less explored. However, this wavelength dependence is of interest, as it contributes to the extinction spectra and is thus readily accessible experimentally. The wavelength dependent scattering can be described by the Mie theory.\textsuperscript{S18} The mathematical framework of this theory is rather complex so that various approximations have been derived. Probably the most well-known approximation is the Rayleigh approximation \textsuperscript{S19}, which describes the scattering coefficient as function of wavelength ($\sigma(\lambda)$) according to equation 1:

$$\sigma(\lambda) = \frac{4\pi^4}{\rho D} \left[ \frac{(n / n_0)^2 - 1}{(n / n_0)^2 + 2} \right]^2 \left( \frac{\lambda}{D} \right)^4$$

(1)

where $D$ is the particle diameter, $\rho$ is the sphere density and $n$ and $n_0$ are the refractive indices inside and outside the sphere (the scattering coefficient is found by dividing the Rayleigh scattering cross-section by the sphere mass). Importantly, equation 1 strictly only holds for spheres with diameters $D<\lambda/10$. When considering molecular solutions with $D<0.5$ nm, the scattering coefficient over the entire spectral region is very small ($<10^{-5}$ L/g m$^{-1}$ with $\rho=1000$ kg/m$^3$, $n=1.5$, $n_0=1.3$) and its contribution to extinction spectra can be neglected. However, this is not the case for colloids.

For larger particles with $D > \lambda/\pi$, the van Hulst approximation\textsuperscript{S20} applies which can also be expressed in the form of the scattering efficient (derivation see \textsuperscript{S21}) according to equation 2:

$$\sigma(\lambda) = \frac{4\pi^2 (n / n_0 - 1)^2}{\rho D} \left( \frac{\lambda}{D} \right)^2$$

(2)

Both approximations show that the wavelength dependent scattering coefficient can be described as a powerlaw with exponents of -4 in the case of particles with diameters $D<\lambda/10$ and -2 for $D > \lambda/\pi$. Accordingly, taking a wavelength of 800 nm, we would expect a scattering exponent, $-m$, of 4 for spheres < 80 nm and 2 for > 250 nm. Importantly, many colloids, such as these investigated here, have intermediate sizes where neither approximation is applicable. As elaborated recently for platelet-like colloids\textsuperscript{S21}, this intermediate particle size regime is characterized by exponents $2<-m<4$ with a strong dependence of the exponent on the nanoparticle projected area. As such, the scattering exponent which is accessible from extinction spectra (Figure S5) can be used as a measure for the particle size of the colloids.
References (SI)

S1 K. Kabsch, in: M. G. Rossmann, E. Arnold (eds.), "International Tables for Crystallography" Vol. F, Ch. 11.3, Kluwer Academic Publishers, Dordrecht, The Netherlands, 2001.

S2 SAINT, Bruker AXS GmbH, Karlsruhe, Germany 1997-2019.

S3 CrysAlisPro, Agilent Technologies UK Ltd., Oxford, UK 2011-2014 and Rigaku Oxford Diffraction, Rigaku Polska Sp.z o.o., Wroclaw, Poland 2015-2019.

S4 R. H. Blessing, Acta Cryst. 1995, A51, 33–38.

S5 (a) G. M. Sheldrick, SADABS, Bruker AXS GmbH, Karlsruhe, Germany 2004-2014; (b) L. Krause, R. Herbst-Irmer, G. M. Sheldrick, D. Stalke, J. Appl. Cryst. 2015, 48, 3–10.

S6 SCALE3 ABSPACK, CrysAlisPro, Agilent Technologies UK Ltd., Oxford, UK 2011-2014 and Rigaku Oxford Diffraction, Rigaku Polska Sp.z o.o., Wroclaw, Poland 2015-2019.

S7 W. R. Busing, H. A. Levy, Acta Cryst. 1957, 10, 180–182.

S8 (a) G. M. Sheldrick, SHELXD, University of Göttingen and Bruker AXS GmbH, Karlsruhe, Germany 2000-2013; (b) G. M. Sheldrick, H. A. Hauptman, C. M. Weeks, R. Miller, I. Ussón, Ab initio phasing, in: M. G. Rossmann, E. Arnold (eds.) International Tables for Crystallography, Vol. F, pp. 333–351, IUCr and Kluwer Academic Publishers, Dordrecht, The Netherlands, 2001.

S9 (a) M. C. Burla, R. Caliandro, B. Carrozzini, G. L. Cascarano, C. Cuocci, C. Giacovazzo, M. Mallamo, A. Mazzzone, G. Polidori, SIR2014, CNR IC, Bari, Italy, 2014; (b) M. C. Burla, R. Caliandro, B. Carrozzini, G. L. Cascarano, C. Cuocci, C. Giacovazzo, M. Mallamo, A. Mazzzone, G. Polidori, J. Appl. Cryst. 2015, 48, 306–309.

S10 (a) L. Palatinus, SUPERFLIP, EPF Lausanne, Switzerland and Fyzikální ústav AV ČR, v. v. i., Prague, Czech Republic, 2007-2014; (b) L. Palatinus, G. Chapuis, J. Appl. Cryst. 2007, 40, 786–790.

S11 (a) G. M. Sheldrick, SHELXL-20xx, University of Göttingen and Bruker AXS GmbH, Karlsruhe, Germany 2012-2018; (b) W. Robinson, G. M. Sheldrick in: N. W. Isaaks, M. R. Taylor (eds.) “Crystallographic Computing 4”, Ch. 22, IUCr and Oxford University Press, Oxford, UK, 1988; (c) G. M. Sheldrick, Acta Cryst. 2008, A64, 112–122; (d) G. M. Sheldrick, Acta Cryst. 2015, C71, 3–8.

S12 (a) J. S. Rollett in: F. R. Ahmed, S. R. Hall, C. P. Huber (eds.) „Crystallographic Computing“ p. 167, Munksgaard, Copenhagen, Denmark, 1970; (b) D. Watkin in: N. W. Isaaks, M. R. Taylor (eds.) „Crystallographic Computing 4”, Ch. 8, IUCr and Oxford University Press, Oxford, UK, 1988; (c) P. Müller, R. Herbst-Irmer, A. L. Spek, T. R. Schneider, M. R. Sawaya in: P. Müller (ed.) “Crystal Structure Refinement”, Ch. 5, Oxford University Press, Oxford, UK, 2006; (d) D. Watkin, J. Appl. Cryst. 2008, 41, 491–522.

S13 A. Thorn, B. Dittrich, G. M. Sheldrick, Acta Cryst. 2012, A68, 448–451.

S14 (a) P. v. d. Sluis, A. L. Spek, Acta Cryst. 1990, A46, 194–201; (b) A. L. Spek, Acta Cryst. 2015, C71, 9–18.

S15 (a) A. L. Spek, PLATON, Utrecht University, The Netherlands; (b) A. L. Spek, J. Appl. Cryst. 2003, 36, 7–13.
F. Foschi, T. Roth, M. Enders, H. Wadepohl, E. Clot, L. H. Gade, *Chem. Commun.* **2018**, *54*, 2228–2231.

H. N. Frock, Particle Size Determination Using Angular Light Scattering. In *Particle Size Distribution*, American Chemical Society: 1987; Vol. 332, pp 146–160.

G. Mie, *Annalen der Physik* **1908**, 330, 377–445.

L. X. Rayleigh, On the electromagnetic theory of light. *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science* **1881**, *12*, 81–101.

H. C. Hulst, *Light Scattering by Small Particles*. Dover Publications: New York, 1981.

A. Harvey, C. Backes, J. B. Boland, X. He, A. Griffin, B. Szydlowska, C. Gabbett, J. F. Donegan, J. N. Coleman, *Nat. Commun.* **2018**, *9*, 4553.