Synthesis, structural, electrochemical and photophysical studies on triferrocenyl-substituted 1,3,5-triphenylbenzene: A cyan-light emitting molecule showing aggregation-induced enhanced emission

Artur Kasprzak*^a, Piotr A. Guńka^a, Agata Kowalczyk^b and Anna M. Nowicka^b

^a Faculty of Chemistry, Warsaw University of Technology, Noakowskiego Str. 3, 00-664 Warsaw, Poland

corresponding author e-mail: akasprzak@ch.pw.edu.pl

^b Faculty of Chemistry, University of Warsaw, Pasteura Str. 1, 02-093 Warsaw, Poland

Electronic Supporting Information (ESI)

Table of contents

S1.	Fluorescence spectra of 3	2
S2.	NMR spectra	4
S3.	IR spectrum of 3	5
S4.	HRMS data on 3	6
S5.	Crystal structure analysis of 3	7
S6.	UV-Vis spectrum of 3	10
S7.	DLS analysis	11
S8.	Powder X-ray diffraction study	12
S9.	References	13

S1. Fluorescence spectra of 3



Figure S1. Emission spectra of **3** in CHCl₃ solution ($2 \cdot 10^{-6}$ M) and single crystal of **3**.



Figure S2. Concentration-dependent emission spectra of 3 in CHCl₃ solution.



Figure S3. Time-dependent emission intensity change of the aggregated **3** in CHCl₃:CH₃OH mixture ($2 \cdot 10^{-6}$ M; solvent with f(CH₃OH) = 0.9).

S2. NMR spectra



220 210 200 190 180 170 160 150 140 130 120 110 100 90 ppm

Figure S5. ¹³C NMR (CDCl₃, 125 MHz) spectrum of 3.

S3. IR spectrum of 3



Figure S6. FT-IR (ATR) spectrum 3.

S4. HRMS data on 3



Figure S7. HRMS (TOF) spectrum of 3 (top: measured, bottom: calculated).

S5. Crystal structure analysis of 3

Crystals of compound **3** suitable for X-ray diffraction analyses were obtained by slow evaporation from a methylene chloride-acetonitrile mixture. A suitable crystal was selected under a microscope using polarized light, glued to a cactus needle using twocomponent epoxy glue and mounted on the goniometer head of a four-circle κ-geometry Gemini A Ultra Rigaku Oxford Diffraction diffractometer. Diffraction data were collected at room temperature using Mo Ka X-ray radiation generated by a sealed tube. CrysAlis^{PRO} program was used for data collection and data reduction.^[1] The selected crystal, as well as other crystals which we measured, turned out to be pseudomerohedrally twinned and the found twin law was 180° rotation around [100] direction in reciprocal lattice with the computed twin ratios of 0.54 : 0.46. The structure was solved and refined using SHELXT and SHELXL programs invoked from within Olex2 suite.^{[2]-[4]} All non-hydrogen atoms were refined with anisotropic displacement parameters, whereas hydrogen atoms were placed at calculated positions. Due to strong thermal vibrations a lot of thermal ellipsoids were elongated and had to be restrained with "ISOR 0.01 0.01" restraints and a lot of bonds were refined with "SADI 0.001" restraints. Table S1 contains X-ray diffraction measurement and crystal structure refinement details. CCDC 2004930 contains supplementary crystallographic data for this paper. These data can be obtained free of charge from the joint CCDC's and FIZ Karlsruhe's service to view and retrieve structures via https://www.ccdc.cam.ac.uk/structures/.

Identification code	3			
Empirical formula	C57H45Fe3N3			
Formula weight	939.51			
T/K	293(2)			
Crystal system	monoclinic			
Space group	P21/c			
a/Å	27.514(3)			
b/Å	6.0470(6)			
c/Å	26.880(4)			
β/°	101.630(12)			
V/Å ³	4380.5(9)			
Ζ	4			
<i>ρ</i> _{calc} /g·cm ^{−3}	1.425			
μ/mm^{-1}	1.024			
<i>F</i> (000)	1944.0			
Crystal size/mm ³	0.26 × 0.056 × 0.034			
Radiation	Μο Κα (λ = 0.71073)			
2O range for data collection/°	6.90 to 50.33			

Table S1	. Crysta	al data	and	structure	refinement	for	3
		i uulu	and	Structure	10 million long	101	J

	<i>−</i> 32 ≤ <i>h</i> ≤ 32,		
Index ranges	$-7 \le k \le 7,$		
	-32 ≤ / ≤ 32		
Reflections collected	8602		
Indonandant reflections	8602 [$R_{int} = 0.224, R_{sigma} =$		
independent reflections	0.2182]		
Data/restraints/parameters	8602/1060/568		
Goodness-of-fit on <i>F</i> ²	0.933		
Final <i>R</i> indexes $[I \ge 2\sigma(I)]$	$R_1 = 0.0949, wR_2 = 0.1686$		
Final <i>R</i> indexes [all data]	$R_1 = 0.1931, wR_2 = 0.1980$		
Largest diff. peak/hole / eÅ ⁻³	+0.95/-0.53		



Figure S8. View of two twin domains of compound **3** along crystallographic [010] direction. The dashed line denotes composition plane perpendicular to twin axis ([100]* direction in reciprocal space). Molecules are shown in ball-and-stick model and colored according to symmetry operation. Hydrogen atoms are omitted for clarity.



Figure S9. Absorbance spectrum of **3** (CHCl₃, $2 \cdot 10^{-5}$ M) and single crystal of **3**.

S7. DLS analysis



Figure S10. Size distribution diagram for **3** in CHCl₃-CH₃OH ($2 \cdot 10^{-6}$ M) with f_{CH3OH} = 0.9.

S8. Powder X-ray diffraction study



Figure S11. Powder diffraction pattern of aggregates of compound **3** (black line) together with a calculated powder diffraction pattern of substance **3** based on crystal structure determined from single-crystal X-ray diffraction experiment (red line).

S9. References

- [1] CrysAlisPro Software System Ver. 171.40.79a; Rigaku OD: Oxford, UK, 2020.
- [2] G. M. Sheldrick. Acta Crystallogr. Sect. A, 2015, 71, 3–8.
- [3] G. M. Sheldrick. Acta Crystallogr. Sect. C, 2015, 3–8.
- [4] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann. *J. Appl. Crystallogr.*, **2009**, *42*, 339–341.