Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Assigning a Structural Motif using Spontaneous Dipole Orientation in Thin Films

M. Roman, A. Dunn[(a)], S. Taj, Z. G. Keolopile[(b)], A. Rosu-Finsen[(c)],
M. Gutowski, and M. R. S. McCoustra,
Institute of Chemical Sciences, Heriot-Watt University, EDINBURGH, EH14 4AS, UK

A. M. Cassidy and D. Field,
Department of Physics and Astronomy, University of Aarhus, AARHUS, DK-8000, Denmark

(a) Current Address: Q2 Solutions, Alba Campus, Rosebank, LIVINGSTON, West Lothian, EH54 7EG, UK;
(b) Department of Physics, University of Botswana, Private Bag 0022, GABORONE, Botswana;
(c) Current Address: Department of Chemistry, University College London, LONDON, WC1H 0AJ, UK.

Table S1. The CCSD/ATZ geometries of the *cis*-, *trans*-MF and the transition state structures.

***cis*-MF**			
C	-0.929000	-0.082997	0.000000
O	0.000951	0.874271	0.000000
O	-0.717913	-1.264024	0.000000
C	1.353536	0.393117	0.000000
H	-1.922975	0.372000	0.000000
H	1.978242	1.280400	0.000000
H	1.538450	-0.208706	0.887518
H	1.538450	-0.208706	-0.887518

***trans*-MF**			
C	0.056643	0.000000	-0.013646
O	-0.025727	0.000000	1.325694
O	1.096774	0.000000	-0.598417
C	-1.354346	0.000000	1.854421
H	-0.924197	0.000000	-0.513131
H	-1.248248	0.000000	2.934380
H	-1.896950	0.893158	1.542933
H	-1.896950	-0.893158	1.542933

***TS*-MF**			
C	0.003861	-0.000182	0.008209
O	0.015538	0.012450	1.437947
O	1.272161	0.002919	1.964765
C	1.889690	0.987458	2.231775
H	1.648170	-1.012162	2.149353
H	-1.039376	-0.033213	-0.289944
H	0.473788	0.903011	-0.382914
H	0.519810	-0.883281	-0.377950

Table S2. Harmonic (H) vibrational constants, anharmonic (AH) corrections to the 0-1 transition, and anharmonic 0-1 transitions (cm^{-1}) followed by the IR intensities (km/mol) of *cis*-MF. δMP2(AH) stands for an anharmonic correction obtained at the MP2 level. All results obtained with the ATZ basis set.

Mode	**Vibrational Constant**					**IR Intensity**
	CCSD(H)	**MP2(H)**	**MP2(AH)**	**δMP2(AH)**	**CCSD(H)+ δMP2(AH)**	**CCSD(H)**
1	155.4	154.5	135.5	-19.0	**136.4**	0.164
2	312.6	307.9	315.2	7.3	**319.9**	14.550
3	340.7	346.4	335.7	-10.7	**330.0**	27.608
4	786.7	771.6	761.6	-10.0	**776.8**	7.797
5	970.0	953.2	925.9	-27.3	**942.7**	27.366
6	1069.7	1046.4	1024.9	-21.6	**1048.1**	0.008
7	1196.7	1187.1	1162.3	-24.8	**1171.9**	1.931
8	1213.3	1192.9	1161.5	-31.4	**1181.9**	62.976
9	1269.4	1246.7	1207.1	-39.6	**1229.8**	279.542
10	1420.0	1399.4	1370.7	-28.8	**1391.2**	1.446
11	1492.8	1478.3	1442.4	-35.9	**1456.8**	3.677
12	1514.6	1511.9	1468.9	-42.9	**1471.7**	8.616
13	1523.3	1519.2	1473.7	-45.5	**1477.8**	10.931
14	1827.0	1769.5	1738.5	-31.0	**1796.0**	316.746
15	3081.1	3096.6	3001.9	-94.7	**2986.4**	25.222
16	3107.5	3111.4	2963.7	-147.7	**2959.8**	36.917
17	3160.8	3189.7	3051.7	-138.1	**3022.7**	15.504
18	3191.1	3224.6	3086.2	-138.4	**3052.6**	11.079

Table S3. Harmonic (H) vibrational constants, anharmonic (AH) corrections to the 0-1 transition, and anharmonic 0-1 transitions (cm^{-1}) followed by the IR intensities (km/mol) of *trans*-MF. δMP2(AH) stands for an anharmonic correction obtained at the MP2 level. All results obtained with the ATZ basis set.

Mode	**Vibrational Constant**					**IR Intensity**
	CCSD(H)	**MP2(H)**	**MP2(AH)**	**δMP2(AH)**	**CCSD(H)+ δMP2(AH)**	**CCSD(H)**
1	40.1	-50.7	-71.5	-20.9	**19.2**	7.414
2	174.3	179.2	175.1	-4.1	**170.2**	1.969
3	352.8	348.0	360.6	12.6	**365.4**	141.963
4	647.9	635.0	627.5	-7.5	**640.4**	1.388
5	1059.4	1036.9	1017.1	-19.9	**1039.5**	0.933
6	1065.2	1043.4	1019.8	-23.6	**1041.6**	234.124
7	1162.8	1142.1	1112.6	-29.4	**1133.4**	1.042
8	1193.6	1183.5	1166.8	-16.7	**1176.9**	5.985
9	1278.2	1256.1	1230.1	-26.0	**1252.2**	0.360
10	1437.5	1415.6	1383.3	-32.3	**1405.2**	20.454
11	1503.2	1488.0	1455.2	-32.8	**1470.4**	7.454
12	1525.6	1522.9	1478.6	-44.2	**1481.4**	405.418
13	1528.2	1525.9	1483.4	-42.5	**1485.7**	0.174
14	1869.1	1807.1	1778.5	-28.5	**1840.6**	38.966
15	3016.5	3013.4	2889.5	-124.0	**2892.5**	40.889
16	3060.0	3079.3	2989.0	-90.2	**2969.8**	23.006
17	3132.2	3168.1	3031.3	-136.8	**2995.4**	55.745
18	3184.6	3216.3	3074.1	-142.2	**3042.4**	8.864

Table S4. Harmonic (H) vibrational constants, anharmonic (AH) corrections to the 0-1 transition, and anharmonic 0-1 transitions (cm^{-1}) followed by the IR intensities (km mol^{-1}) of *TS*-MF. δMP2(AH) stands for an anharmonic correction obtained at the MP2 level. All results obtained with the ATZ basis set.

Mode	**Vibrational Constant**					**IR Int**
	CCSD(H)	**MP2(H)**	**MP2(AH)**	**δMP2(AH)**	**CCSD(H)+ δMP2(AH)**	**CCSD(H)**
1	-232.2	-242.4	-243.4	-1.1	**-233.2**	14.480
2	170.2	184.0	173.0	-10.9	**159.3**	0.521
3	303.8	290.1	289.3	-0.8	**303.0**	5.064
4	675.4	661.6	651.9	-9.7	**665.7**	20.398
5	992.5	974.8	952.3	-22.5	**970.0**	44.521
6	1064.5	1045.5	1026.0	-19.5	**1045.0**	36.210
7	1171.6	1146.4	1110.7	-35.7	**1135.9**	208.809
8	1188.6	1179.1	1153.1	-26.0	**1162.6**	11.495
9	1245.9	1226.2	1196.2	-29.9	**1216.0**	120.412
10	1410.4	1391.0	1359.3	-31.8	**1378.7**	2.892
11	1497.8	1485.3	1450.5	-34.8	**1463.0**	1.926
12	1520.9	1518.7	1474.5	-44.2	**1476.7**	8.031
13	1531.8	1529.6	1487.2	-42.4	**1489.4**	8.461
14	1848.5	1780.7	1748.6	-32.1	**1816.4**	286.013
15	3041.7	3044.9	2900.0	-144.9	**2896.8**	39.191
16	3048.9	3058.2	2989.8	-68.4	**2980.6**	51.320
17	3116.5	3143.4	3010.2	-133.3	**2983.3**	24.463
18	3178.2	3205.6	3068.8	-136.9	**3041.3**	11.741

Table S5. Harmonic MP2/ADZ frequencies in D1-D3 determined on the counterpoise-corrected potential energy surface.

	Frequency / cm^{-1}			
	D1	**D2**	**D3**	***cis*-MF**
1	17.3303	19.0039	16.7124	
2	26.4705	30.538	36.8971	
3	42.5924	39.0231	49.9524	
4	47.6156	58.0936	54.0311	
5	57.7024	75.6491	64.8637	
6	70.0688	83.4757	78.1731	
7	162.4087	166.1605	165.7097	163.968
8	187.3773	192.491	166.2273	
9	305.1273	304.7949	311.9271	305.348
10	305.2332	311.9556	312.1476	
11	344.4287	346.9061	350.5635	342.917
12	345.1247	352.9687	354.996	
13	760.2241	760.8088	759.7379	760.597
14	762.6378	763.8339	764.0251	
15	926.388	926.0598	935.4404	935.337
16	927.075	936.8103	937.1531	
17	1032.8117	1033.3412	1051.2394	1029.946
18	1033.0014	1051.8451	1052.4327	
19	1155.4815	1170.7097	1169.4609	1171.054
20	1157.5565	1172.5636	1170.793	
21	1171.9672	1175.2556	1170.8236	1173.481
22	1176.1757	1180.652	1177.1273	
23	1228.4044	1222.2935	1217.6592	1222.217
24	1232.2351	1237.2636	1229.5588	
25	1385.6053	1386.3478	1384.8582	1382.523
26	1385.6997	1391.4834	1388.2572	
27	1442.1982	1449.3153	1449.5398	1450.475
28	1442.2528	1455.6981	1449.5713	
29	1471.3311	1480.4056	1480.493	1480.569
30	1478.939	1485.615	1480.5013	
31	1483.0065	1487.4534	1487.3872	1487.800
32	1483.576	1498.1259	1487.5147	
33	**1733.1417**[b]	**1727.1686**[b,d]	**1722.0303**[b]	**1743.977**[a]
34	**1743.6041**[c]	**1741.5904**[c,e]	**1735.4076**[c]	
35	3105.9356	3091.6806	3092.7908	3093.263
36	3106.0578	3092.3399	3092.8931	
37	3122.6878	3124.5049	3152.9848	3125.711
38	3123.0755	3156.2131	3153.5715	
39	3211.7238	3191.3952	3192.2235	3192.902
40	3212.8546	3197.7573	3192.247	
41	3236.6277	3227.6137	3228.092	3228.845
42	3237.3012	3229.7349	3228.1109	

[a]This mode of *cis*-MF is dominated by the C=O stretch; [b]symmetric; [c]antisymmetric; [d]dominated by monomer 1; [e]dominated by monomer 2

Table S6. The energies of D2 and D3 with respect to D1 at various levels of theory (all energies in meV).

	D2	**D3**
E_{HF}^{∞}	-33.44	-51.74
E_{MP2}^{∞}	37.02	63.18
ΔE_{CCSD}	7.93	14.58
ΔE_{T}	-3.05	-5.24
E_{total}	8.46	20.79
E_{0}^{vib}	1.93	-7.13
$E_{total} + E_{o}^{vib}$	10.40	13.66

Table S7. Structure of one-body deformation energy for two cis monomers in D1-D3. (All energies in meV).

	1@D1	**2@D1**	**1@D2**	**2@D2**	**1@D3**	**2@D3**
E_{HF}^{∞}	1.25	1.25	9.87	1.55	9.13	9.13
E_{MP2}^{∞}	0.79	0.79	-5.25	2.37	-4.46	-4.46
ΔE_{CCSD}	0.54	0.54	1.16	0.15	1.00	1.00
ΔE_{T}	-0.28	-0.28	-1.14	-0.19	-1.02	-1.02
E_{total}	2.30	2.30	4.64	3.88	4.65	4.65

Table S8. Structure of the two-body interaction energy between deformed monomers in the D1, D2 and D3 dimers (All energies in meV).

	D1	**D2**	**D3**
E_{HF}^{∞}	-80.85	-123.20	-148.33
E_{MP2}^{∞}	-102.37	-60.90	-28.70
ΔE_{CCSD}	-6.88	0.83	6.79
ΔE_{T}	-8.93	-11.21	-12.69
E_{total}	-199.03	-194.47	-182.93

Figure S1. 16 low-energy structures of the MF dimer determined at the MP2/ADZ level. The relative energies in meV. The energies in parentheses obtained on the counterpoise-corrected surface.